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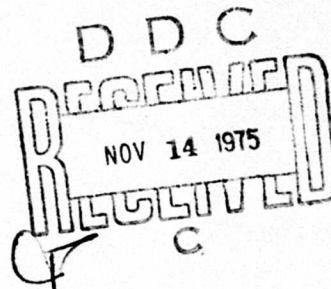
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HIGH RATE, RECHARGEABLE, SILVER-ZINC PILE TYPE BATTERY

EAGLE-PICHER INDUSTRIES, INC.
ELECTRONICS DIVISION
JOPLIN, MISSOURI 64801

MAY, 1975

TECHNICAL REPORT AFAPL-TR-75-51
REPORT FOR PERIOD 1 MAY 1974 - 1 MAY 1975



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This final report was submitted by Eagle-Picher Industries, Inc., under Contract USAF F33615-74-C-2045. The effort was sponsored by the Air Force Aero Propulsion Laboratory, Air Force Systems Command, Wright-Patterson AFB, Ohio under Project 3145, Task 22 and Work Unit 63 with Mr. Dick Marsh/POE-1 as Scientist In Charge. Mr. L. R. Erisman of Eagle-Picher Industries, Inc. was technically responsible for the work.

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This technical report has been reviewed and is approved for publication.

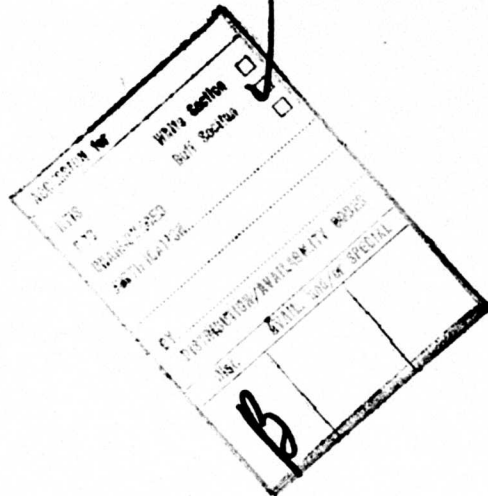
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20. ABSTRACT (Continue on reverse side if necessary and identify by block number) This report describes the work accomplished in the development of a high rate, rechargeable, silver-zinc, pile type battery for the contract period of 1 May 1974 through 1 May 1975. This program is an extension of a preceding study contract, USAF F33615-73-C-2074, and consisted of utilizing component development data to establish processing, fabrication and performance capabilities for a multi-cell pile configuration. A modular system concept using basic 100 kw modules was retained to project accumulated pile test data into systems of the multi-megawatt power range. These studies demonstrated components could be		

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processed and fabricated into submodules capable of assembly into a four (4) megawatt, thirty (30) second system of 3800 pounds and less than 20 cubic feet could be realized.

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1.0 INTRODUCTION

This report is an Interim Technical presentation of work performed in development of a High Power, Rechargeable, Pile Type Silver-Zinc Battery under USAF Contract Number F33615-74-C-2045. The material contained herein has been accumulated during the reporting period from 1 May 1974 to 1 May 1975 and covers establishing component configuration, processing of the same and fabrication and testing of single and multi-cell piles. The major objective of this contract phase was to define the necessary components and fabrication techniques which could be utilized in producing a full scale submodule capable of 200 amperes and an individual cell voltage of 1.20 or better.

2.0 General

The general approach in development of the subject battery was to utilize existing data and experimentally demonstrate their performance when used in a multi-cell pile design. Component studies were continued as a parallel effort to process, fabrication and testing to support further their development as necessary.

Considerable time was consumed during this phase to establish processing capabilities for a full size bipolar electrode. This included not only scaling up from laboratory processes, but actual construction of the full scale equipment.

Trade off studies conducted during this period to determine the module system relationship is best described by Figure 1, which shows the basic design concepts as developed during the past two (2) years. As this figure shows, considerable changes have been made in both the module and system designs. Starting with a basic rectangular module to the present design, which includes a fully designed, both electrically and mechanically, unit with comparisons to potential installations.

The proposed module/system physical breakdown is presented by Figure 2 and shows the relation of cells, submodules and modules to a complete system of three (3) megawatts.

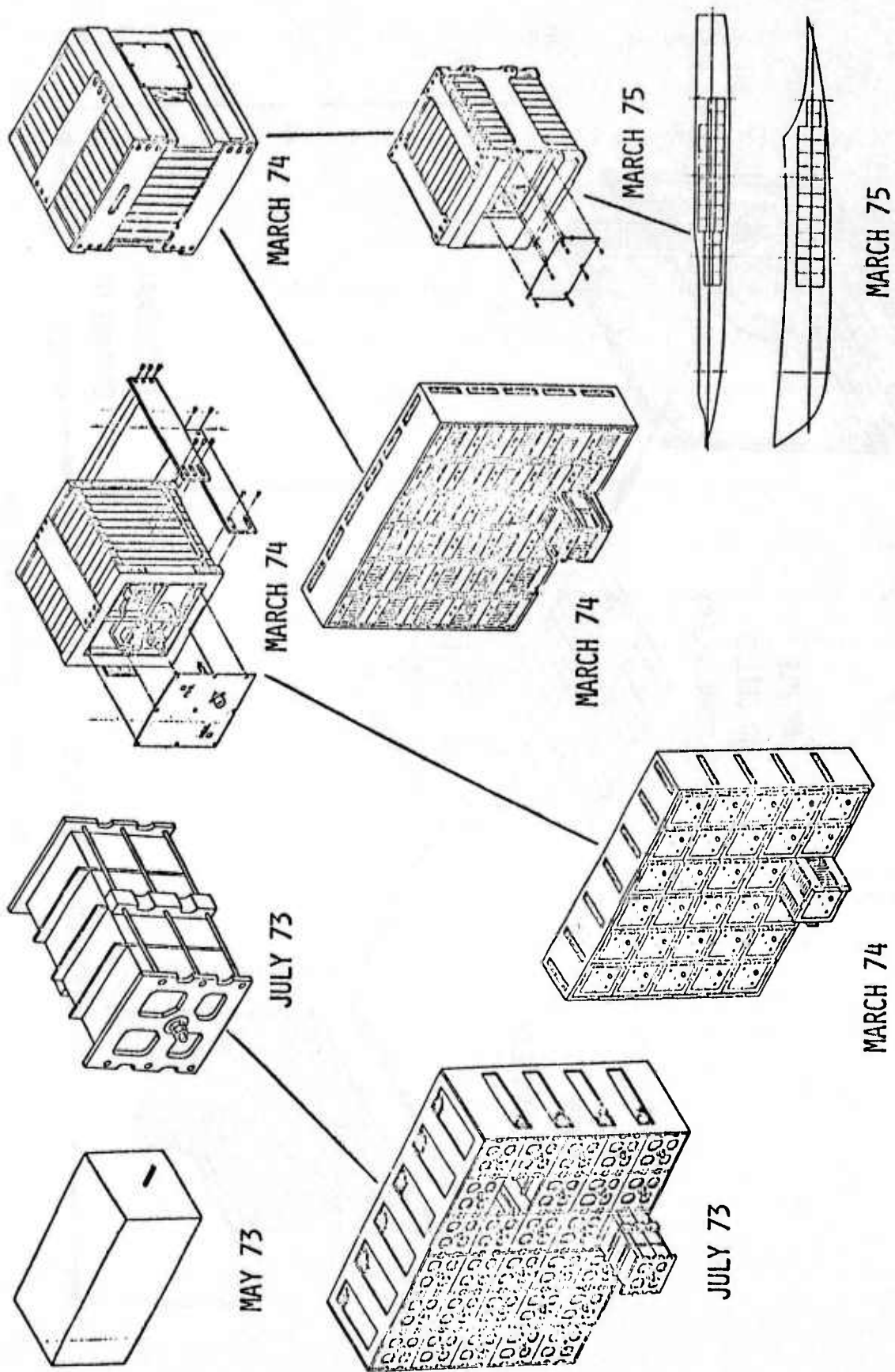


Figure 1 - Design Concept Development

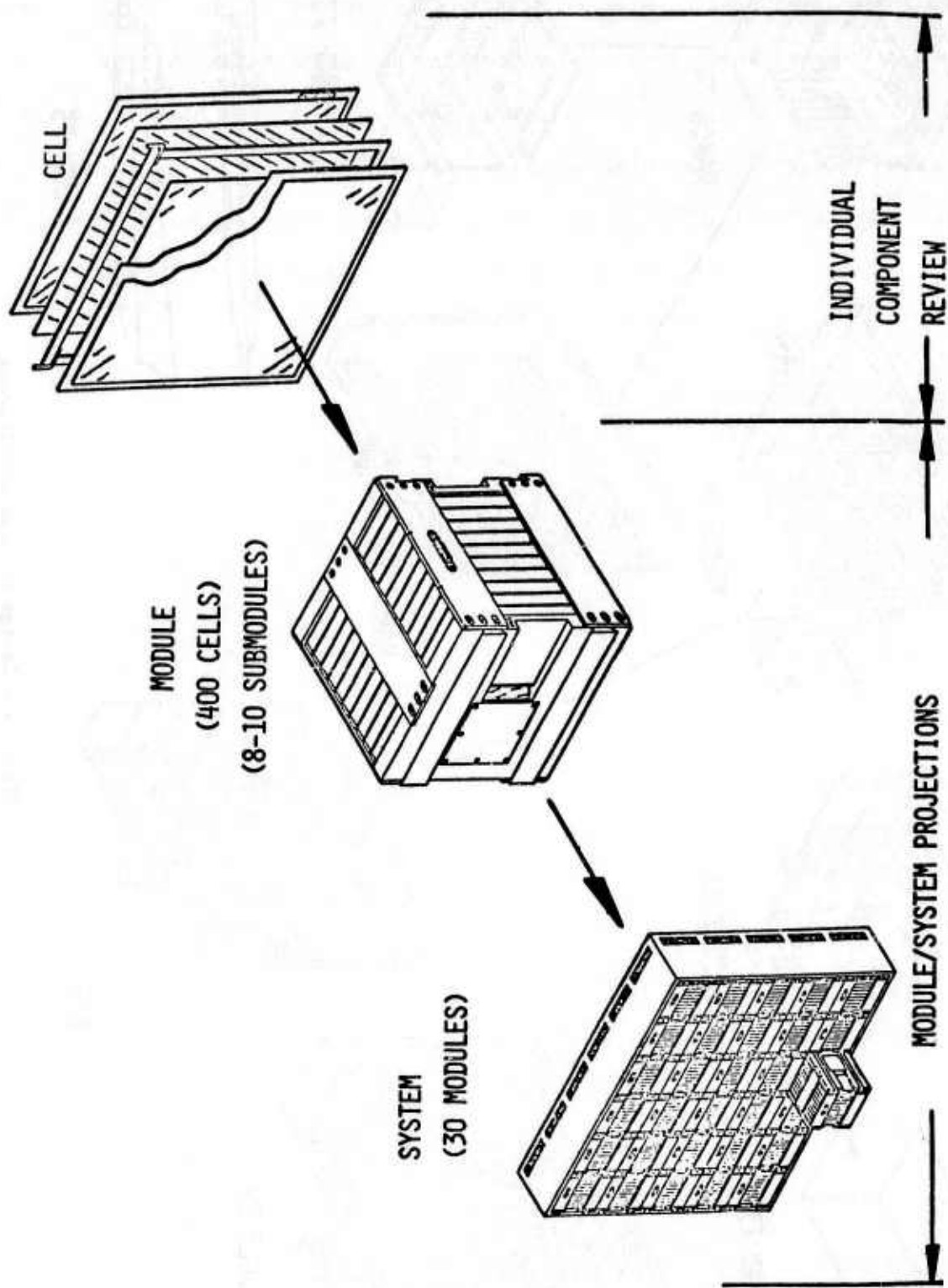


Figure 2 - Module/System Physical Breakdowns

3.0 Individual Component Development

As previously stated, component studies were conducted throughout this phase as a parallel support effort. The individual components as shown by Figure 3 were studied in both laboratory and pile configurations.

The cell design can be broken down into five (5) basic elements; positive side of bipolar electrode, negative side of bipolar electrode, separator, seal and adhesive, and intercell connectors (substrate for bipolar electrode). These elements will be discussed in detail in the following paragraphs.

3.1 Positive Electrode

The positive side of the bipolar electrode has caused less problems than any of the individual components in development of the pile battery. Likewise, during this contract phase, the processing equipment was also of least problems to set up. During the initial study contract, the most promising cell configuration included the use of an uncharged positive electrode, which also simplifies the process by eliminating its electroformation prior to cell fabrication.

The following paragraphs describe the final electrode development, configuration and processing.

3.1.1 Component Development

The primary objectives to be accomplished in producing a viable positive electrode was to attach a porous silver matrix to silver foil of approximately .002 inch thick. The maximum density had previously been found to be 95 grams per cubic inch without sacrificing material utilization. Therefore, a density providing minimum volume, of 80 to 90 grams per cubic inch was set as a process goal. An active material thickness of .0015 inch was also established. This thickness provides an excess of active material, and was found to be a minimum practical amount to process.

The initial process investigations included spraying via a conventional spray gun, and was expanded into the present process setup which is explained in detail in Paragraph 3.1.3.

3.1.2 Configuration

The present configuration of the positive electrode is a sintered, porous silver matrix as shown by SEM photographs of Figures 4 and 5. This material is deposited onto a silver foil substrate which has been previously prepared as described in Paragraph 3.5. The active material distribution is controlled to .12 to .15 grams per square inch at a thickness of .0016 inch. Deposition consists of spraying a slurry of silver oxide and subsequently sintering.

Previous test data has shown that the following Material Utilization for this type electrode is:

<u>Current Density</u>	<u>Material Utilization Factor (MUF)</u>
2.0 amp/in ²	1160 as/gm
1.75 amp/in ²	1200 as/gm
1.5 amp/in ²	1240 as/gm

Assuming a material deposit of .13 gram per square inch, the following information is provided.

<u>Current Density (Amp/In²)</u>	<u>Theoretical Capacity (Amp. Sec/In²)</u>	<u>Practical Capacity (Amp. Sec/In²)</u>	<u>30 Sec. Requirement (Amp. Sec/In²)</u>	<u>Use Efficiency (%)</u>
1.5	232	161	45	28
1.75	232	156	53	34
2.00	232	151	60	40

The above information shows a low utilization of practical capacity with sufficient material to support discharges up to 107, 90, and 75 seconds for rates of 1.5, 1.75 and 2.0 amperes per square inch respectively. This design has been established as a result of processing evaluation and was found to be optimum, consist with the present processing equipment, providing good adhesion and uniform material distribution.

Figure 6 is a drawing of the present bipolar electrode. The active positive material is sprayed over the entire surface of the silver foil extending across the seal area. One (1) end of each submodule requires a half-electrode consisting of porous silver and silver foil only. The foil utilized on this electrode is .010 inch thick to provide additional current distribution cross sectional area and increase physical strength resistance. Figure 7 is a drawing of the end electrode.

The chemical makeup of the complete positive electrode is shown by the following spectrographic analysis.

<u>Element</u>	<u>Percent</u>
Sn	.02
Fe	.0005
Mg	.002
Al	.----
Cu	.0005
Ag	Major
Na	.01
Ca	.02

3.1.3 Processing

Processing of the positive side of the bipolar electrode has been set up in such a manner that it can be used in a continuous line. However, since only a limited number of electrodes are required for this phase of the contract, the equipment is used as a piece part setup. The processing equipment is divided into three (3) separate sections, each designed for continuous operation. They are:

1. Spray deposition
2. Drying/Sintering
3. Pressing

The above equipment is shown by Figures 8, 9 and 10. Capabilities of this setup provide a capability of depositing onto foil a porous matrix of silver ranging from .1 to 1.0 gram per square inch at densities from 40

to maximum grams per cubic inch. The present process rate is approximately 100 electrode per hour with continuous potential of 600. Expanding to 1200 electrodes could easily be achieved by only the addition of drying oven sections.

The spraying operation consists of a vented spray booth with a conventional paint spray head mounted over a continuous belt and is shown by Figures 8 and 11. The spray head is microswitch activated as the continuous belt feeds single electrode foil positioned on a rack. The rack is fabricated from woven nickel screen allowing overspray to go through without damaging the sprayed foil by over or under running.

The drying/sintering oven is constructed from 22-11 x 22 inch infrared heating modules as shown by Figures 9 and 12. The modules are positioned so that drying or sintering is accomplished from both the top and bottom. The first seven (7) modules are adjusted so that the temperature is limited to approximately 300°F providing a zone for drying. The sintering is performed in the next zone of 4 modules where the temperature reaches approximately 900°F.

Pressing of the electrodes is performed by two (2) four (4) in diameter rollers. The bottom roller is permanent while the top floats under a controllable pressure. The roller press is shown by Figures 10 and 13.

Starting with foil which has completed surface preparation as described in Paragraph 3.5, the positive active material is deposited in accordance with the following procedure.

1. Blend mix 45% H₂O - 2400 gms
 54% Ag₂O - 2910 gms
 1.0% C.M.C. - 54 gms (sulfur free)

2. Pour H_2O into blender, add C.M.C. and blend for a minimum of ten (10) minutes.
3. Add Ag_2O blend for a minimum of one (1) hour.
4. Pour mix into tank of spray gun, tighten lid, adjust tank pressure to $20 \pm .5$ p.s.i.
5. Adjust spray nozzle atomizing air to $32 \pm .5$ p.s.i.
6. Place etched silver foil to be sprayed onto spray rack.
7. Place spray rack with foil onto a support plate and place on conveyor belt.
8. Set control on conveyor to 60% of full speed (approximately 14 feet per minute).
9. Turn conveyor belt on, spray positive plate.
10. Remove spray rack and plate from opposite end of conveyor and place into drying oven.
11. Set voltage on drying oven at 150-175 volts (approximately 300°F).
12. Remove spray rack and plate when deposited mix is visibly dry (approximately 45 seconds). Each plate should be covered by 18-22 grams of silver oxide. Adjust settings of steps 4, 5, or 8 if necessary.
13. Place dried plates into sintering oven for twenty (20) seconds (approximately 900°F).
14. Inspect each plate for physical appearance.
15. Set air pressure at 80 psi on press and roll sintered plates once.
16. Finished plates should weigh .12-.15 gm/sq. in. with a density of 70-90 gm/in³. Reject all plates above or below this range.
17. Final plate weights should be recorded on the back side of each plate in one corner next to the foil weight.

The acceptable positive electrodes are then stored in an enclosed container until ready for the negative deposition as described in Paragraph 3.2.3.

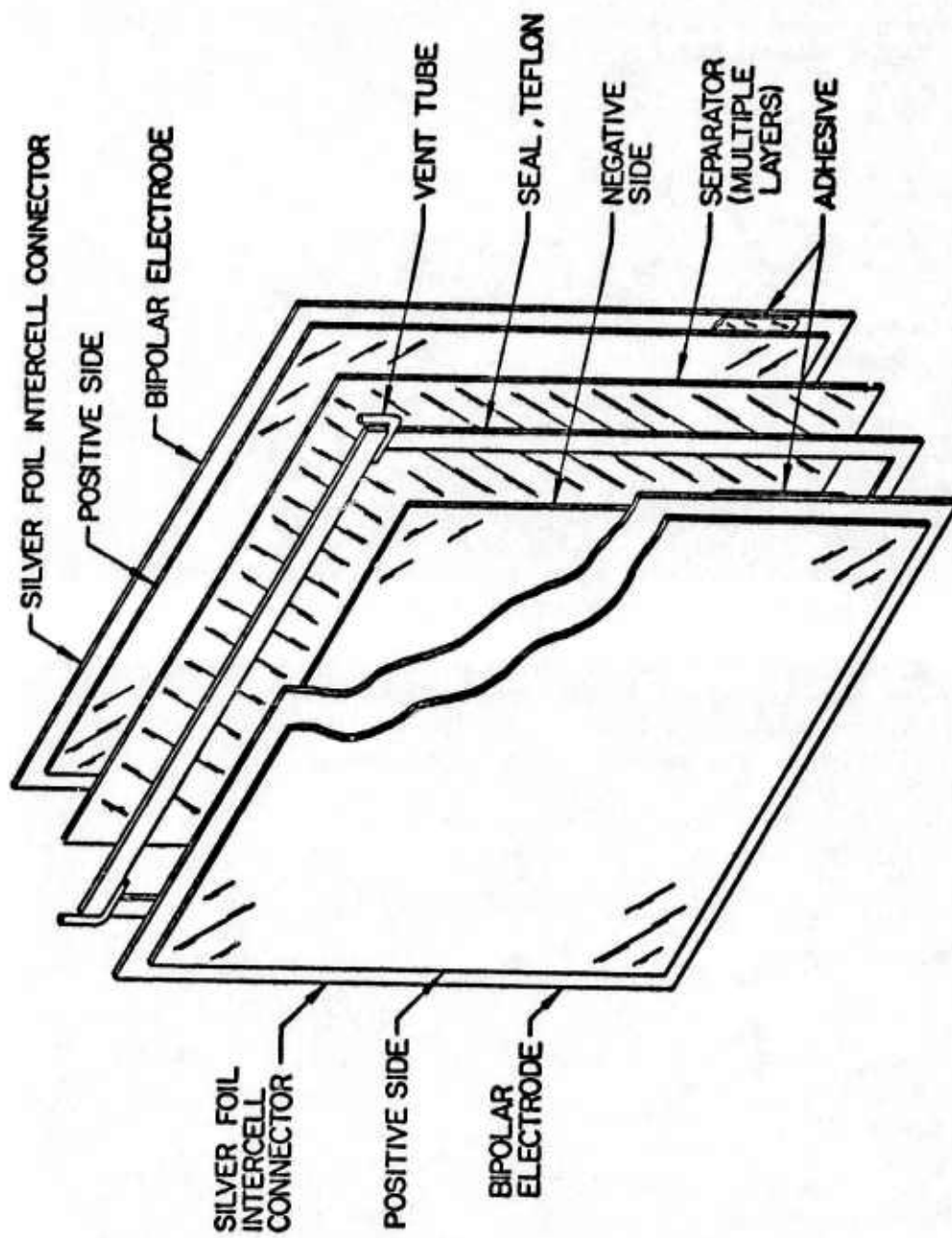


Figure 3 - Relationship of Components

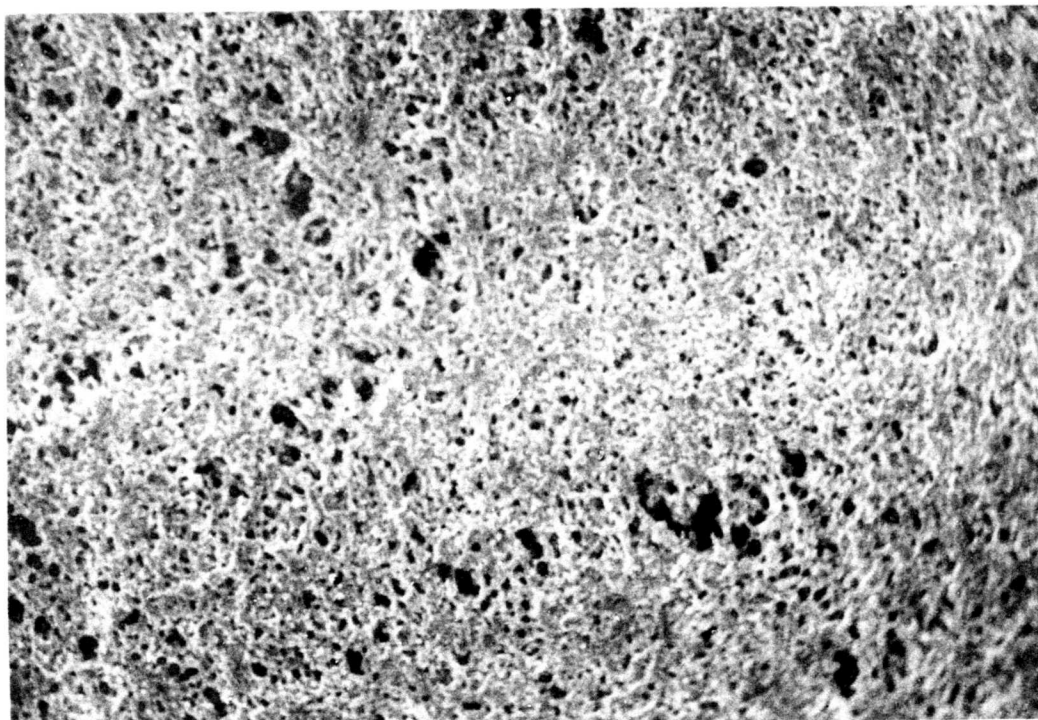


Figure 4 - Positive Electrode Surface - 300X

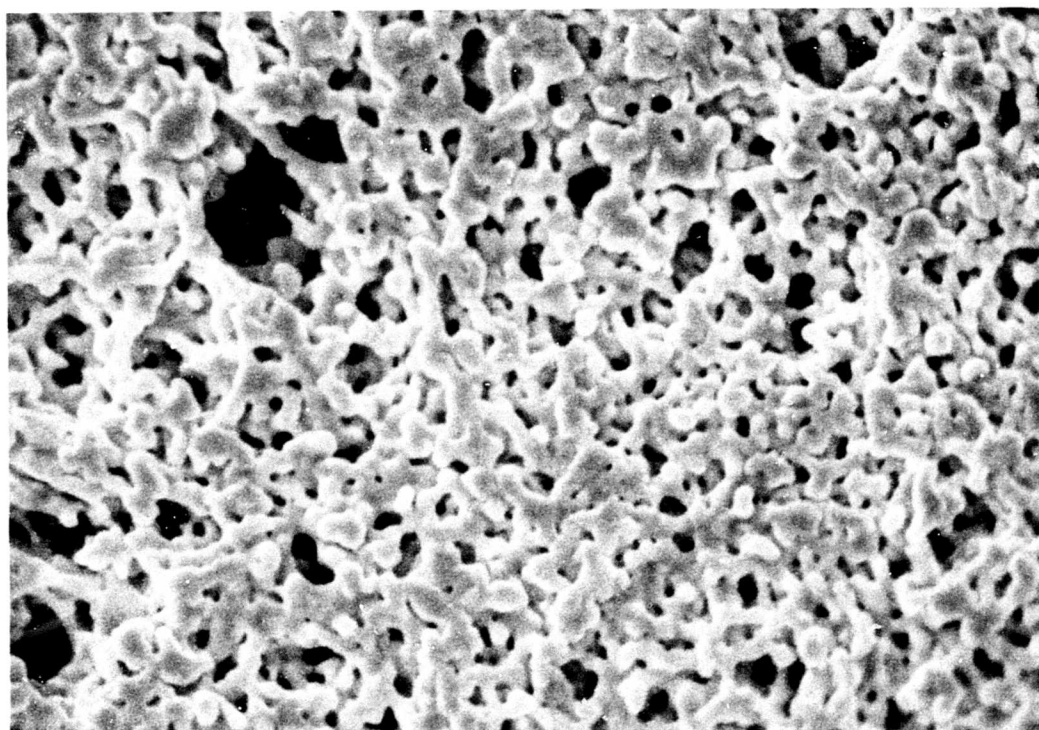
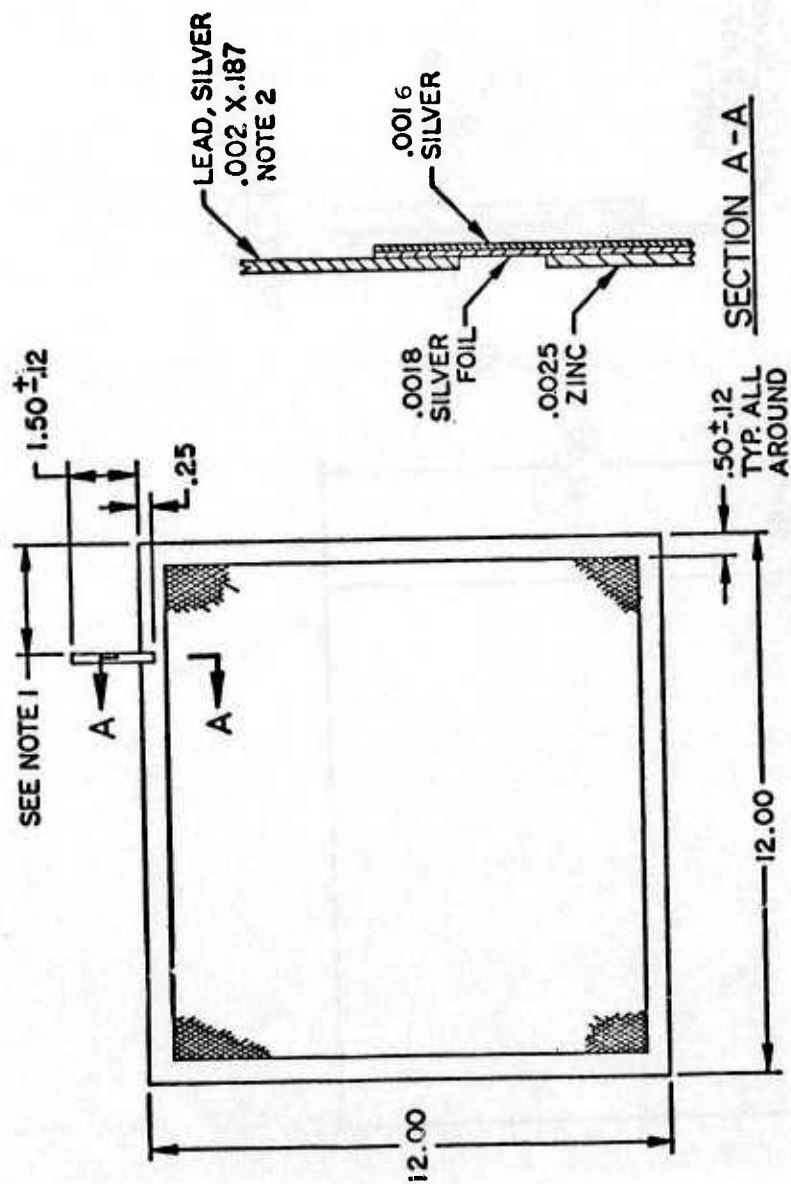


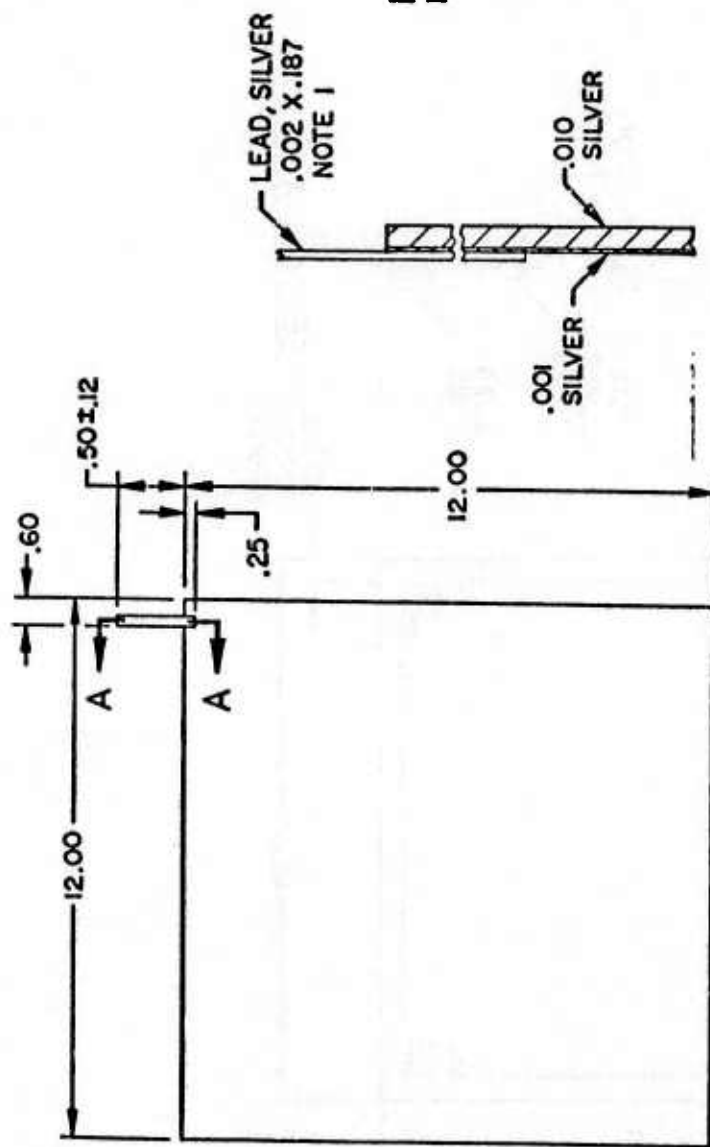
Figure 5 - Positive Electrode Surface - 1000X



NOTES:

1. REFERENCE MWPP-3
2. SPOTWELD LEAD TO PLATE PER MIL-W-6858 USING A MINIMUM OF 3 WELDS.

Figure 6 - Bipolar Electrode



NOTES:

1. SPOTWELD LEAD TO PLATE PER MIL-W-6858 USING A MINIMUM OF 3 WELOS.

SECTION A-A

Figure 7 - Positive End Electrode

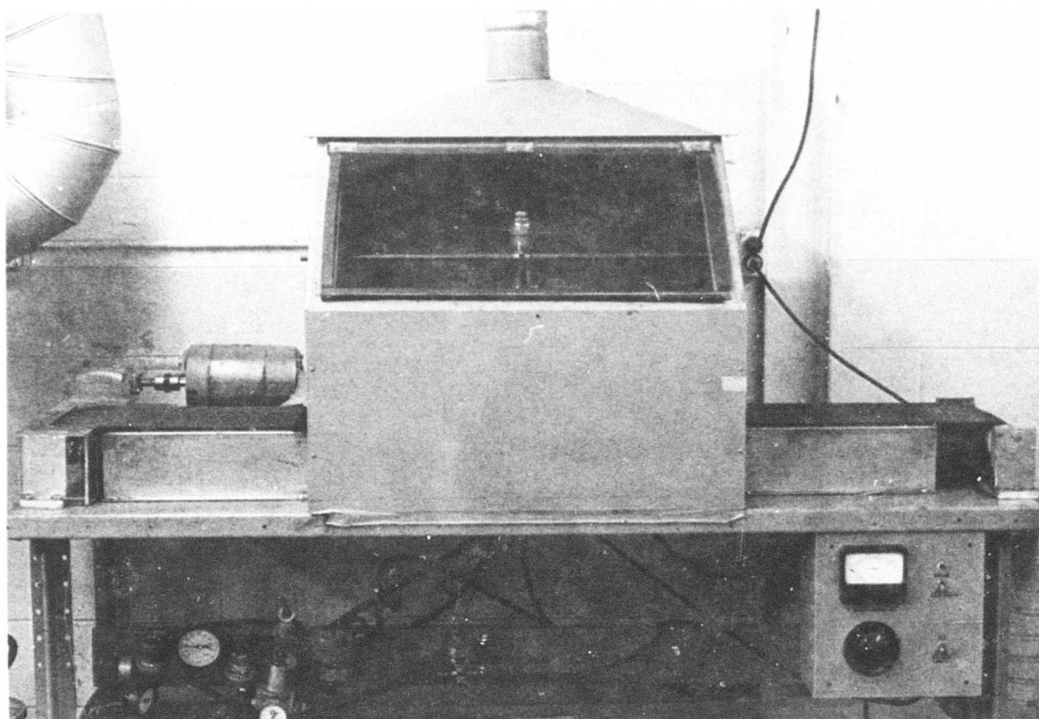


Figure 8 - Positive Electrode - Spray Equipment

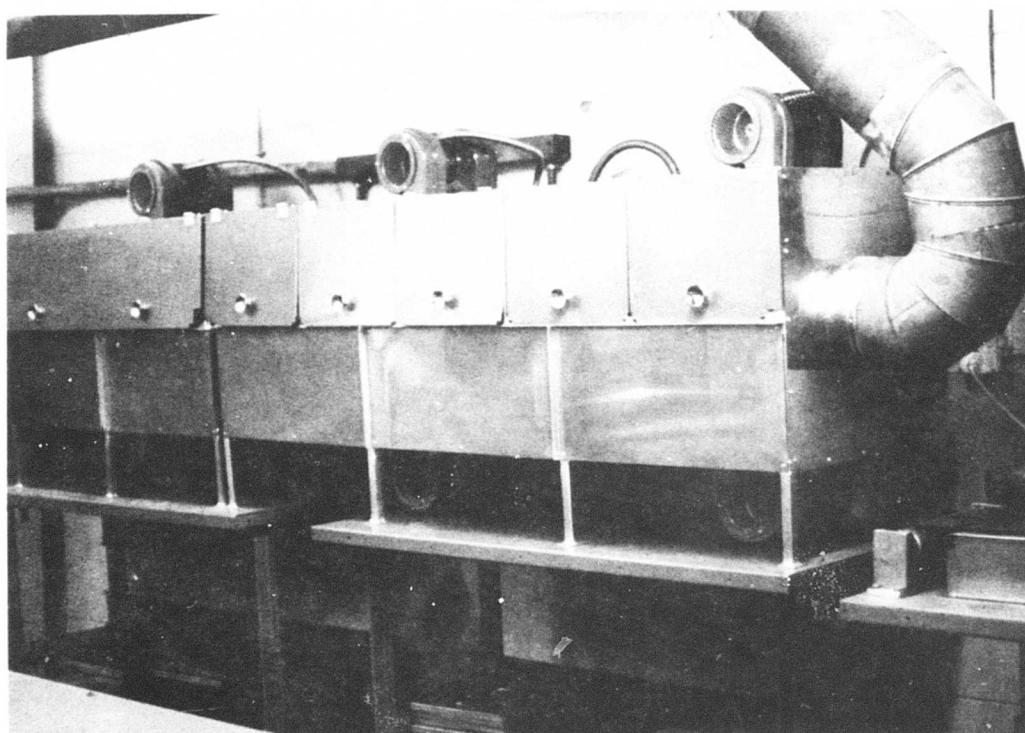


Figure 9 - Positive Electrode - Dry and Sinter Equipment

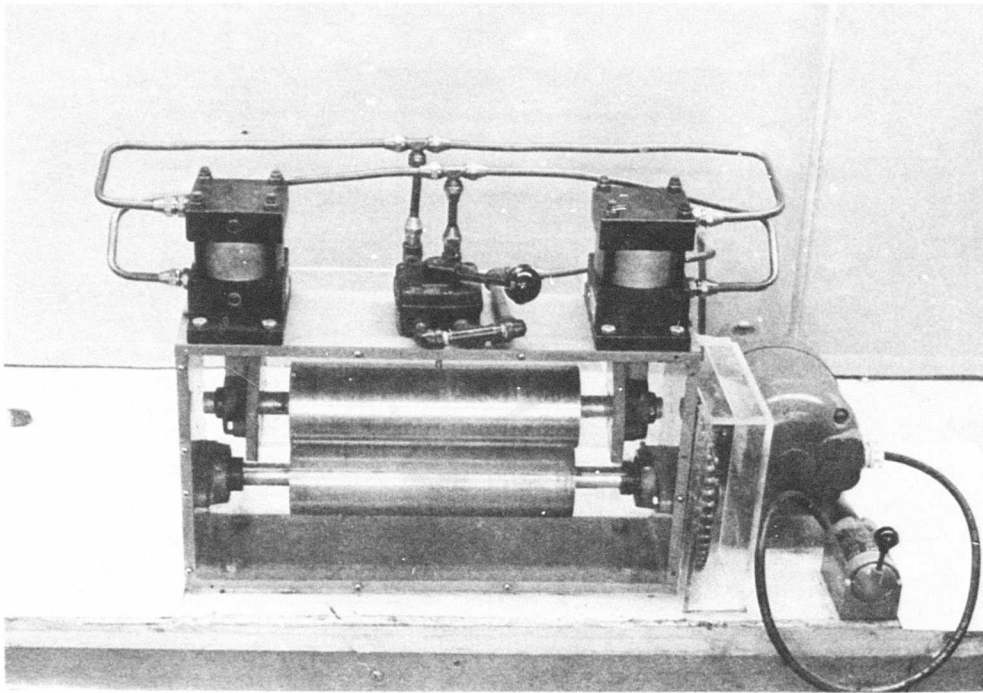


Figure 10 - Positive Electrode - Pressing Equipment

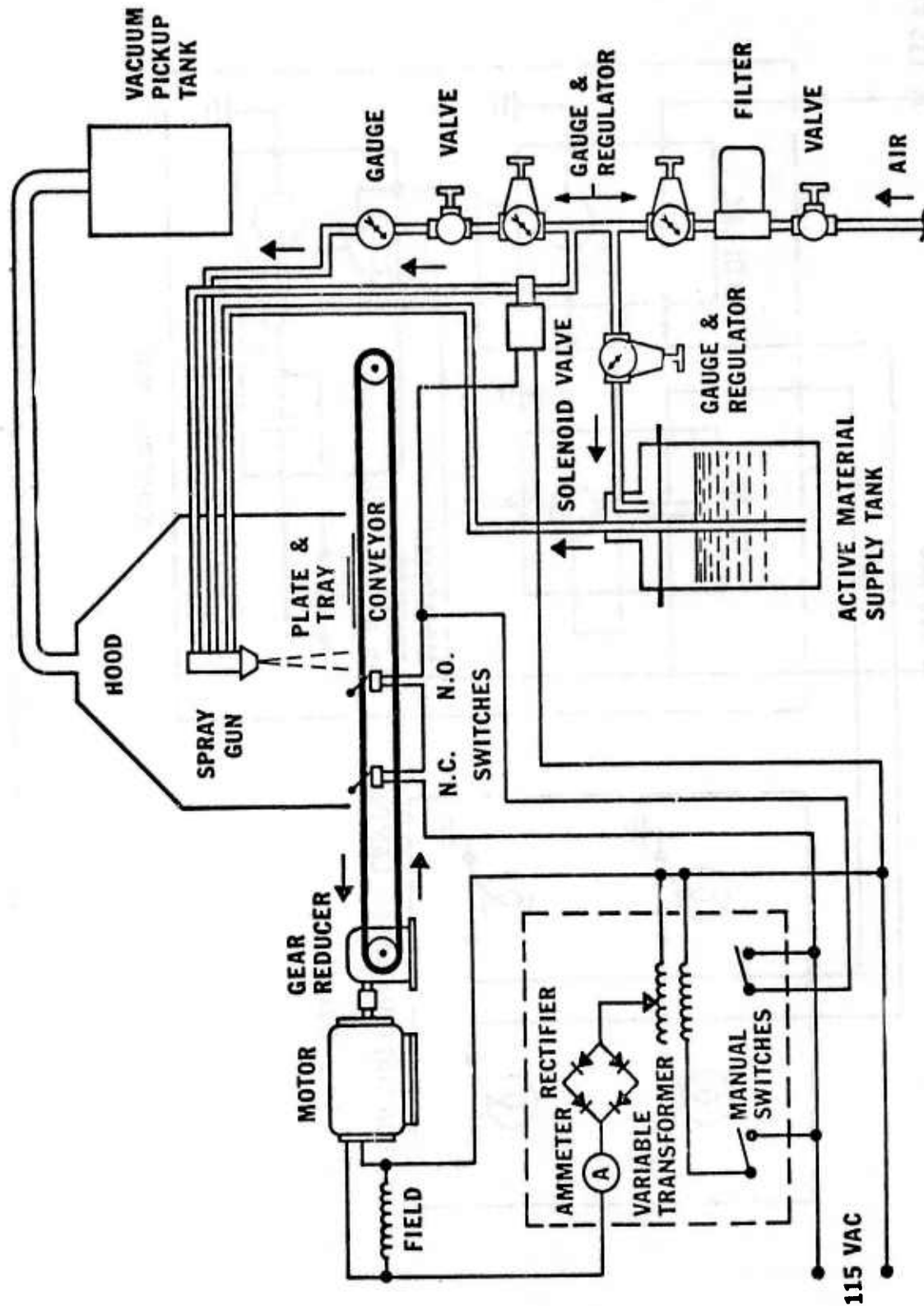


Figure 11 - Positive Electrode - Spray Equipment Diagram

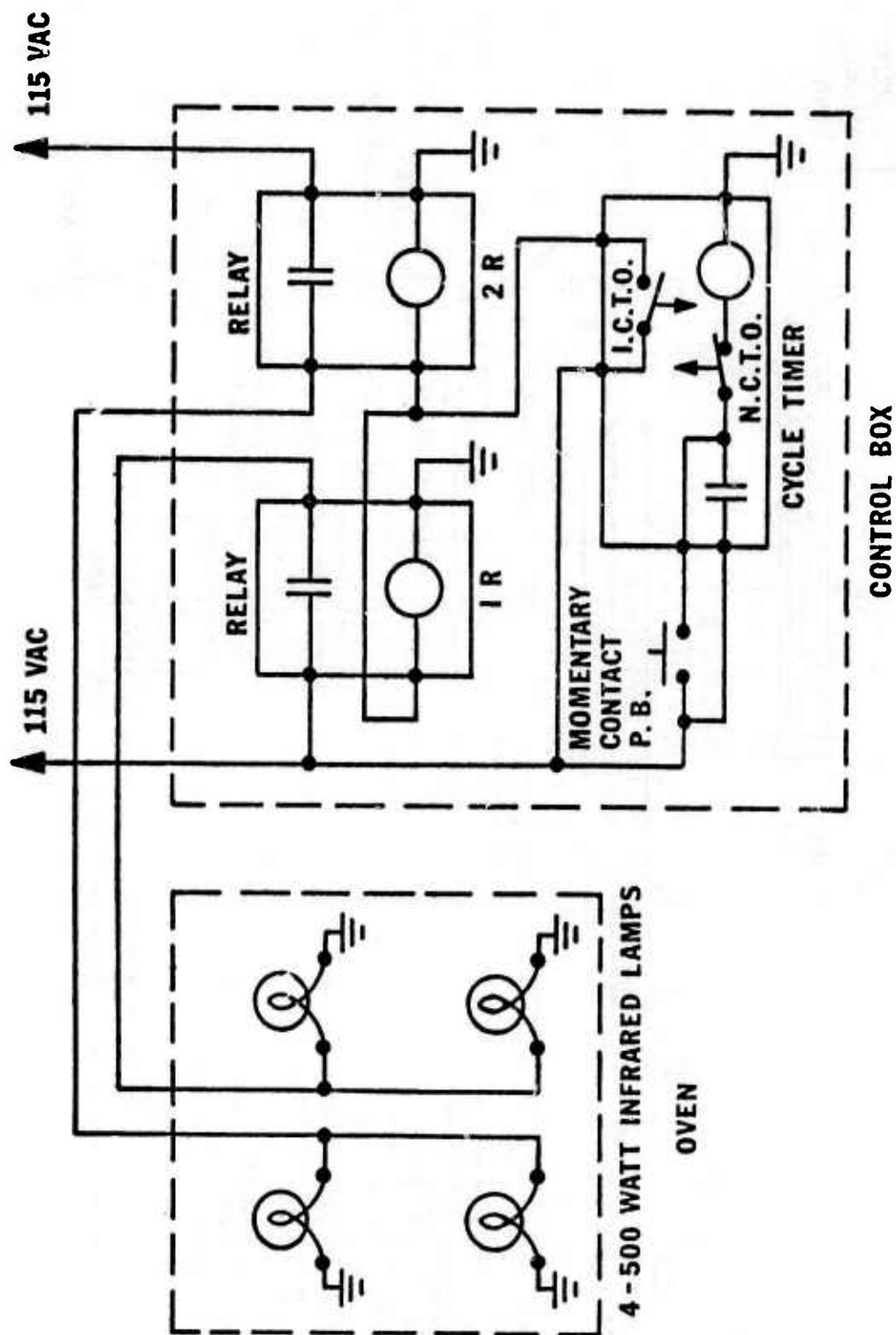


Figure 12 - Positive Electrode - Dry and Sinter Diagram

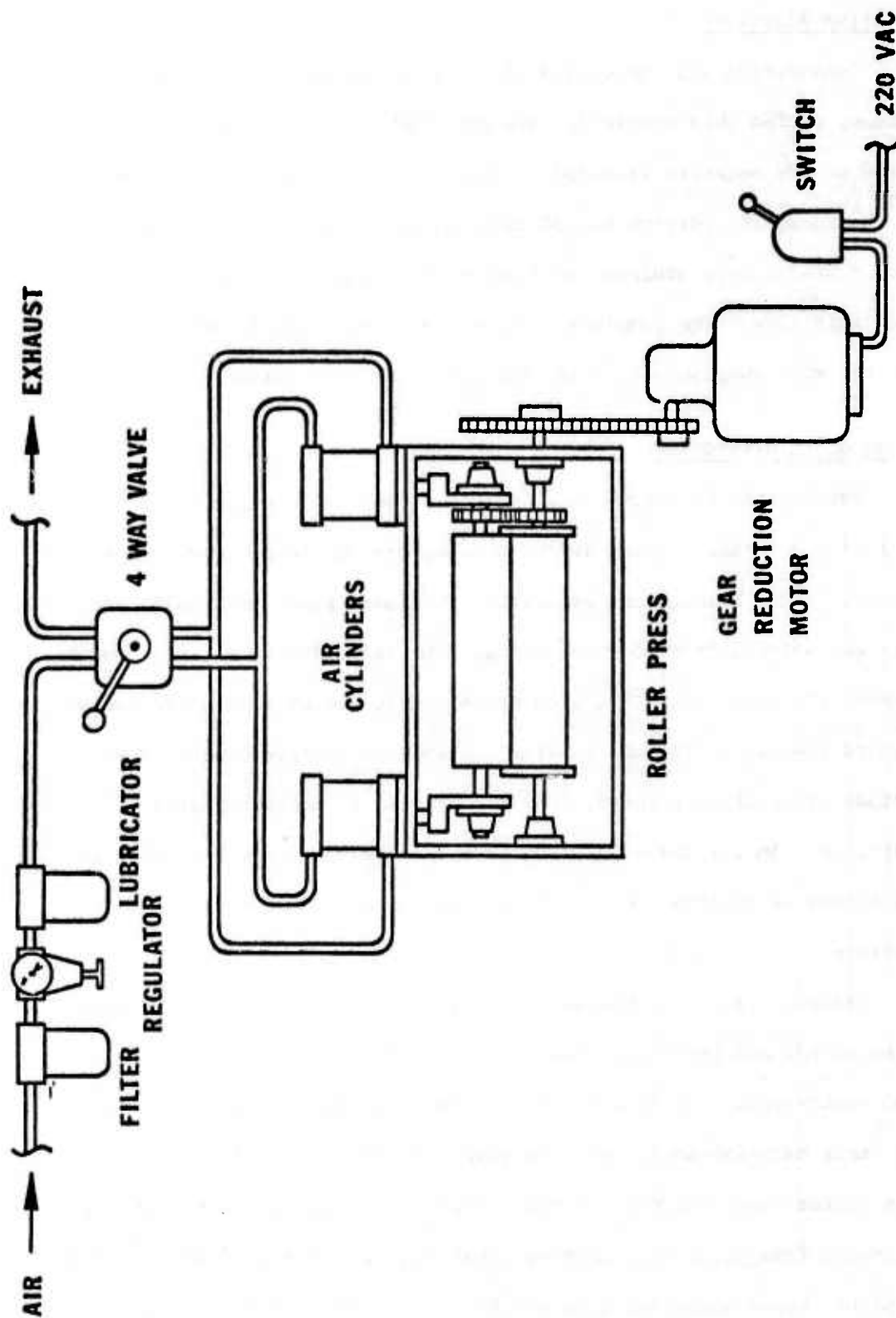


Figure 13 - Positive Electrode - Press Diagram

3.2 Negative Electrode

Considering all components of the pile battery design, the majority of problems, during this contract, have occurred in the configuration and processing of the negative electrode. Since the design of the pile battery is more desirable as a dry-uncharged unit, it is necessary that the negative electrode contain, as a minimum, sufficient zinc oxide to charge the positive electrode initially. The remainder of the active material is most desirable as zinc, and more adaptable to thin film electrode processing.

3.2.1 Component Development

During this contract phase, several types of negative depositions were evaluated. Initial phases included deposition by means of vacuum transfer pasting, doctor blades, and spraying. The basic plate originally evaluated was one which consisted primarily of zinc oxide due to the most desirable counter electrode being sintered silver. The use of zinc oxide lended itself quite readily to vacuum transfer pasting and spraying, as well as doctor blade processing; however, they are limited to thicker plates than desirable. In all three (3) processes, it also was necessary that an inactive binder be utilized to attach the active zinc oxide material to the substrate.

Various mixes were evaluated using different percentages of zinc oxide/zinc blends and was found that approximately 25% zinc oxide blend performed electrically superior to those previously tested. As the evaluation of this material continued, the compatibility to any of the three (3) processes listed above was not the most desirable, since the heavy metallic zinc separates from the slurry mixture, producing a nonhomogenous electrode. At this point, vapor deposited zinc was again reviewed from the standpoint

that electrodes could be produced without the use of the binder material. It is also easier to produce a thin layer of active material, considerably more homogenous than that of the slurry deposited materials. During the evaluation of the vapor deposited zinc, several electrodes were constructed onto which zinc oxide had been sprayed. These plates were subsequently dried and fabricated into test cells and performed equally as well as the totally pasted plates. It was also found that zinc oxide could be introduced to the plate during the vapor deposition process by injecting oxygen into the vacuum chamber during the process. Several test cells were constructed of the vaporized zinc/zinc oxide type resulting in improved overall material utilization. Continuing studies into the controls necessary to producing electrode with a predictable amount of zinc oxide included, showed that variations occurred within the plate as well as plate to plate process, and this approach was discontinued.

The decision was made at that time to utilize the vaporized zinc electrode with a sprayed zinc oxide surface layer. Included in the processing of this electrode was the necessity to scale up from a bell jar setup to a facility capable of producing multiple full size electrodes.

As testing of pile cells progressed, it became quite evident that gases generated internally were detrimental to the performance of the cell operation, and that it was necessary to remove them. Initially, the gases were considered to be formed by improper charging techniques. Various combinations of charge rates and cut off voltages were tried in an attempt to solve internal gas problems. However, these solutions were insufficient and gases were being produced from other phases of the cell operation. Mechanical devices were set up which included both vacuum and pressure to relieve

the cell during the activation, charge and discharge. A combination of mechanical devices, charge rate, and end of charge voltage improved the gasing situation, however, not to the extent that the cell could operate at its fullest potential. The negative electrode was separated from the remainder of the cell components and studied with respect to gases generated from the silver/zinc interface. It was observed during the negative studies that if a sample of the electrode, on silver substrate, was placed in a beaker of potassium hydroxide electrolyte, gasing would occur in two (2) distinct phases. First, within ten (10) seconds of immersion, a fine gasing would occur on the zinc side of the electrode which appeared to be a light smoke. This gas evolution is called "reaction or displacement gas" and continues for a period of approximately one (1) minute at which time large well defined bubbles appear at the silver side of the electrode and are generated quite rapidly for some extended period of time. These gases are the result of the galvanic couple of silver-zinc in a common electrolyte and have been identified as hydrogen, a result of oxidizing the active zinc material through the decomposition of water. This condition of zinc on silver substrate subjected to a common electrolyte does not occur in the actual pile cells. It should, however, be pointed out that the interface between the silver and zinc does exist. In the event that this interface is not completely blocked, the electrolyte may penetrate through the active zinc material to the silver substrate resulting in localized, corrosion sites.

Along with pile configuration testing, observations were made that the seal adhesive/silver foil on the negative side of the electrode interface begins to deteriorate in the presence of potassium hydroxide. It was felt

that both the reaction gases and the local corrosion sites could produce undesirable conditions, resulting in this seal breakdown. Several elements and compounds were considered as additives to the electrolyte as well as various substrate materials to reduce the adverse gasing. A series of tests were conducted to determine the extent of improvement from additives to the electrolyte. These tests were conducted in a closed test cell from which a tube was extended into the graduated burette for collection and quantitative comparison. Samples were placed in 1.35 s. g. potassium hydroxide and allowed to stand at a minimum of two (2) hours. The volumes generated during this period were recorded and the results are listed in Table I. Also, in Table I, it will be found that the additives were also tried with a combination of zinc deposits on copper and zinc intercell connector materials

From negative electrode component studies, it was also found that the vapor deposited zinc electrode possesses a lower negative voltage than that normally associated with zinc electrode. Comparisons were made utilizing a silver oxide counter-electrode. It was suggested that possibly pretreatment of the negative electrode by dipping in potassium hydroxide with a subsequent rinse and dry would increase this lower negative voltage. Results of treating the negative electrode for one (1) minute and three (3) minute periods with various combinations of additives and substrate materials did not show any appreciable change. The only significant improvement found was the combination of active material with zinc oxide substrate which was approximately .010 volt. A combination of the studies performed under this contract and information provided from the USAF Aero Propulsion Laboratory show additions of oxidized cellulose and wetting agents could also improve negative electrode performance. Multi-cell piles and single cells were constructed and tested utilizing a combination of additives and substrate

materials. At the present time, it has been demonstrated physically that reduced gassing does occur with use of stannous chloride, oxidized cellulose, wetting agents and zinc intercell connectors. However, no quantitative values have been established at this time for the pile configuration. Continued studies with these additions in combination with mechanical and electrical variations hopefully will result in a viable negative electrode for the pile type battery.

Figures 14, 15 and 16 show the material utilization factor (MUF) for the selected electrode. These curves have been constructed from test data at current densities of 1.5, 1.75 and 2.0 amps per square inch. For the majority of module/system projections, the median curves have been used and will be considered a point of reference for the remainder of this report. Considering the values shown in Figure 14, the median MUF for 1.5, 1.75 and 2.0 amps/inch² is 650, 680 and 600 respectively. Using these MUF's in the projection program gives a negative electrode of approximately .12 to .14 grams/inch² and a density of 55 to 65 grams/inch³. This corresponds to an electrode of zinc, .002 inch thick, which increases to .0025 after the zinc oxide is applied to the surface. Since the zinc oxide layer is soluble in the electrolyte, only sufficient material is applied to initially charge the positive electrode and is calculated to be approximately .06 gram/inch².

The electrode evaluation described in the preceding paragraph has culminated in a structurally and electrically proven electrode resulting in its use in test cells and piles. Problems have been evident and are contributed mainly to internally generated gases which when compounded with the overall physical configuration, prevents the maximum potential from being exhibited by the negative electrode.

Figures 20 and 21 are SEM photographs showing the zinc/intercell connector cross-section, which is porous throughout extending to the silver substrate.

3.2.2 Component Configuration

The present configuration of the negative electrode consists of vapor depositing onto silver foil, a porous zinc structure. Zinc Oxide is then sprayed on this surface to complete the bipolar electrode. Figures 17, 18, and 19 show the physical structure of vapor deposited zinc by SEM photographs. The silver foil used for the zinc deposition has previously been processed for the positive, with the exposed negative side prepared as described in Paragraph 3.5. The active material is deposited directly onto the silver foil substrate at a material distribution of .12 to .14 grams per square inch with a density of 55 to 56 grams per cubic inch.

The median material utilization factors from Figure 13 are:

2.0 amps/inch ²	600 as/gram
1.75 amps/inch ²	685 as/gram
1.50 amps/inch ²	650 as/gram

Using an active material loading of .13 grams/inch², the following efficiencies may be calculated:

<u>Current Density (Amp/In²)</u>	<u>Theoretical Capacity (Amp. Sec/In²)</u>	<u>Practical Capacity (Amp. Sec/In²)</u>	<u>30 Sec. Requirement (Amp. Sec/In²)</u>	<u>Use Efficiency (%)</u>
2.0	384	78	60	77
1.75	384	89	53	60
1.5	384	84	45	54

The above information shows that the actual use efficiency for a 30 second discharge is high, however, when compared to theoretical capacity, the use is only 15-20 percent. This design has been proven adequate in both component and pile tests to support a thirty (30) second discharge providing all other factors such as gassing are minimum.

Figure 6 is a drawing showing the relation of the negative active material to the bipolar electrode. The zinc is applied only to the active cell area, leaving a foil edge to which the seal is attached. One (1) end of each submodule requires a half-electrode and is shown by Figure 22. Chemical analysis of the vapor deposited material has been shown to be 99,4 percent zinc. A final coat of zinc oxide is applied to complete the electrode by spraying the active material surface with .06 grams/inch².

3.2.3 Component Processing

Processing of the negative electrode side of the bipolar electrode is set up on a batch basis. The present capability can produce 16 electrodes in two (2) hours which is limited by the physical size of the vacuum chamber. Full production could be scaled up either in a batch basis or as a continuous strip. To produce 100 electrodes in a batch process would require a chamber approximately six (6) feet in diameter by six (6) feet long.

The complete processing of the negative electrode is divided into two (2) separate phases, vapor deposition of the zinc and spraying of the zinc oxide.

Figures 23, 24 and 25 show the processing equipment for the negative electrode. Starting with an electrode which has previously been processed as described for the positive side in Paragraph 3.1.3, the negative is deposited by the following procedure:

1. Set controls on 220 volt powerstat at 80% to premelt zinc.
2. Place 8 each 18-22 gm positive plates (electrodes) on deposition drum, active material face down.
3. Install electrode masking bands onto drum over silver foil exposing only the area to be deposited.

4. Clean electrodes on drum with M.E.K. after bands are installed.
5. Pour 500 gms molten zinc into 13" carbon source boats.
6. Place boats on heater assembly inside vacuum chamber.
7. Move loaded drum of step 3 into position inside vacuum chamber.
8. Position stainless cover over carbon boats.
9. Align door coupling on drum, close door, tighten clamps around door.
10. Open vacuum valve on control console.
11. Start vacuum pumps.
12. Start drum drive motor 60 r.p.m.
13. Pump vacuum chamber ambient down to 20-40 microns to start glow discharge.
14. Turn on high voltage power supply and adjust to 450 volts @ 450 ma for 15 minutes.
15. Turn off glow discharge and backfill with nitrogen to 2000 microns.
16. Start heater power supply set at 275 volts, 12.5 amps. Record every five (5) minutes; temperature, voltage and amperage.
17. After 35 minutes, remove stainless cover from carbon boats.
18. Deposit zinc for 9 to 10 minutes maintaining vacuum at 2000 microns and heaters at 275 volts, 12.5 amps.
19. Turn off heater and adjust nitrogen flow to 50 c.f.h. for 10 minutes, then to 150 c.f.h. until chamber pressure is equalized to ambient.
20. Remove drum from chamber, remove masking bands and electrodes from drum.
21. Finished negative active material should weigh .12 to .14 gm/sq. in. with a density of 55 to 65 gm/inch³. Any negatives above or below these ranges will be rejected.

22. Identify each acceptable electrode by a consecutive number.
23. Record foil weight, positive weight (gm/inch²), negative weight (gm/inch²) and negative density (gm/inch³) on data sheet.

After each electrode has been inspected, the following procedure is used to deposit the zinc oxide surface coat. The equipment for this process is identical to that used in spraying the positive electrode (Reference Paragraph 3.1.3):

1. Clean seal area on both sides of the bipolar electrode using MEK solvent.
2. Locate and spotweld tabs to positive side of bipolar electrodes, one tap per bipolar electrode. Using tab locator fixture 14, start with first tab on left and work to the right placing completed electrode in a stack, positive side down. Each electrode will be separated from adjacent electrode by a plate divider.
3. Using the adhesive dispenser system, prime seal area on both sides of bipolar electrode.
4. Oven dry primed bipolar electrodes at 130°F for 1.5 hours.
5. Mix ZnO/Additives blend per the following formula:

73.9% H ₂ O - 600 gms	.7% HgO - 6 gms
24.6% ZnO - 200 gms	.7% Microthene - 6 gms
6. Attach chipboard mask to negative side of bipolar electrodes.
7. Spray active zinc material with ZnO/Additives blend.
8. Place bipolar electrodes with wet ZnO/Additive blend in an oven set at 300°F for 30 minutes to cure binder and dry ZnO.
9. Using MEK solvent, clean seal area on both sides of the bipolar electrode.
10. Weigh and record weight. The ZnO/Additive blend should weigh 0.06 ± .02 grams per square inch.

11. Flat press each bipolar electrode to an 8 mil shimmed thickness using 1000 psig.
12. Store bipolar electrodes on trays with plate dividers and cover to avoid contamination.

TABLE I - ELECTROLYTE ADDITIVE/SUBSTRATE GAS COMPARISON

Substrate Material	Sample Size (In ²)	KOH (Ml)	Electrolyte Additive		Collection Time (Hrs)	Total Gas Collected (Ml)
			Type	(Gms)		
Ag	4.5	150	ZnO	Saturated	2	2
Ag	4.5	150	---	---		40
Ag			SnCl ₂	3		5
Ag			LiOH	3		6
Ag			CdO	3		12
Zn			---	---		2
Zn			SnCl ₂	3		1.5
Zn			LiOH	3		1.5
Zn			CdO	3		---
Cu			---	---		8
Cu			SnCl ₂	3		1.5
Cu			LiOH	3		1.5
Cu			CdO	3		---

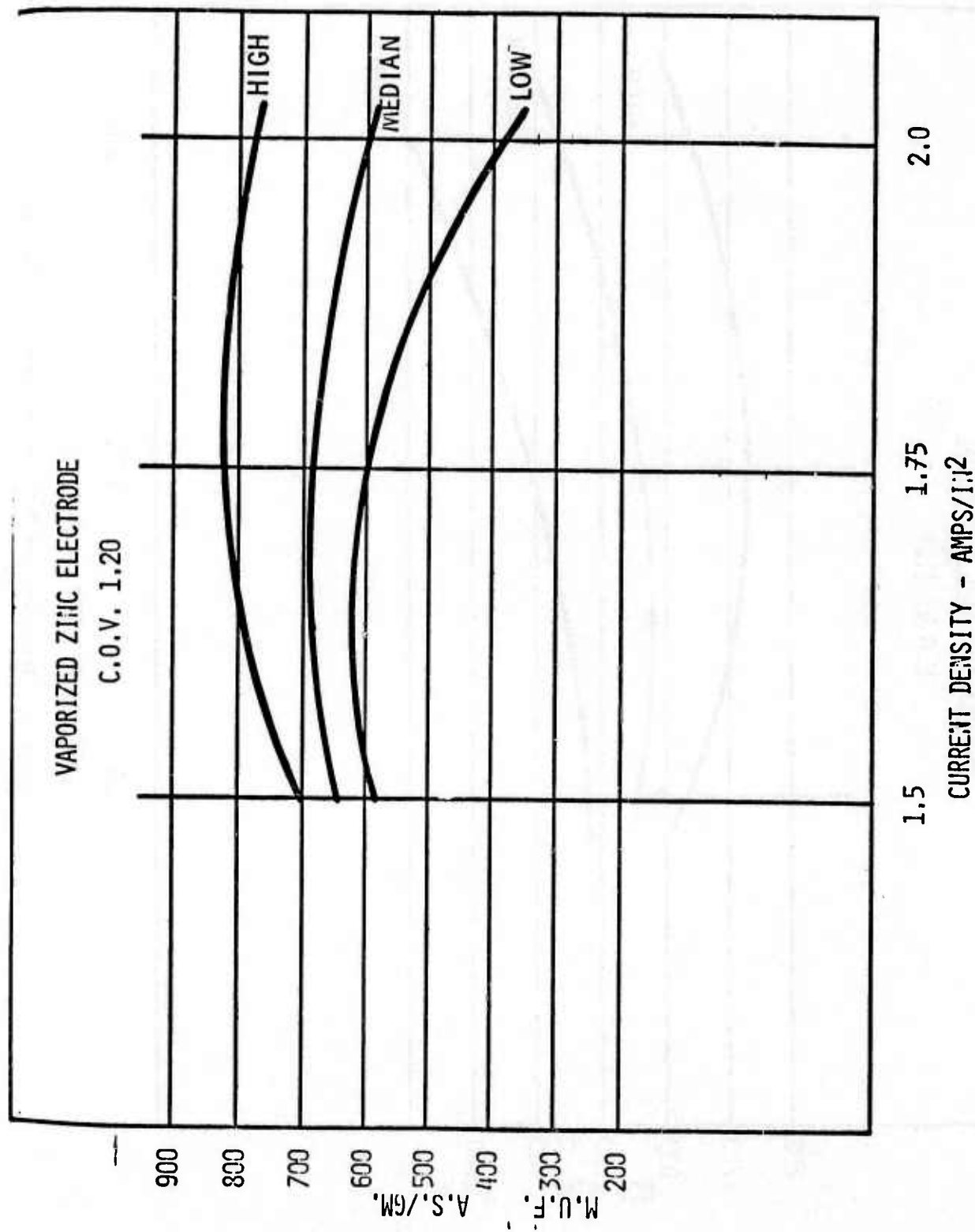
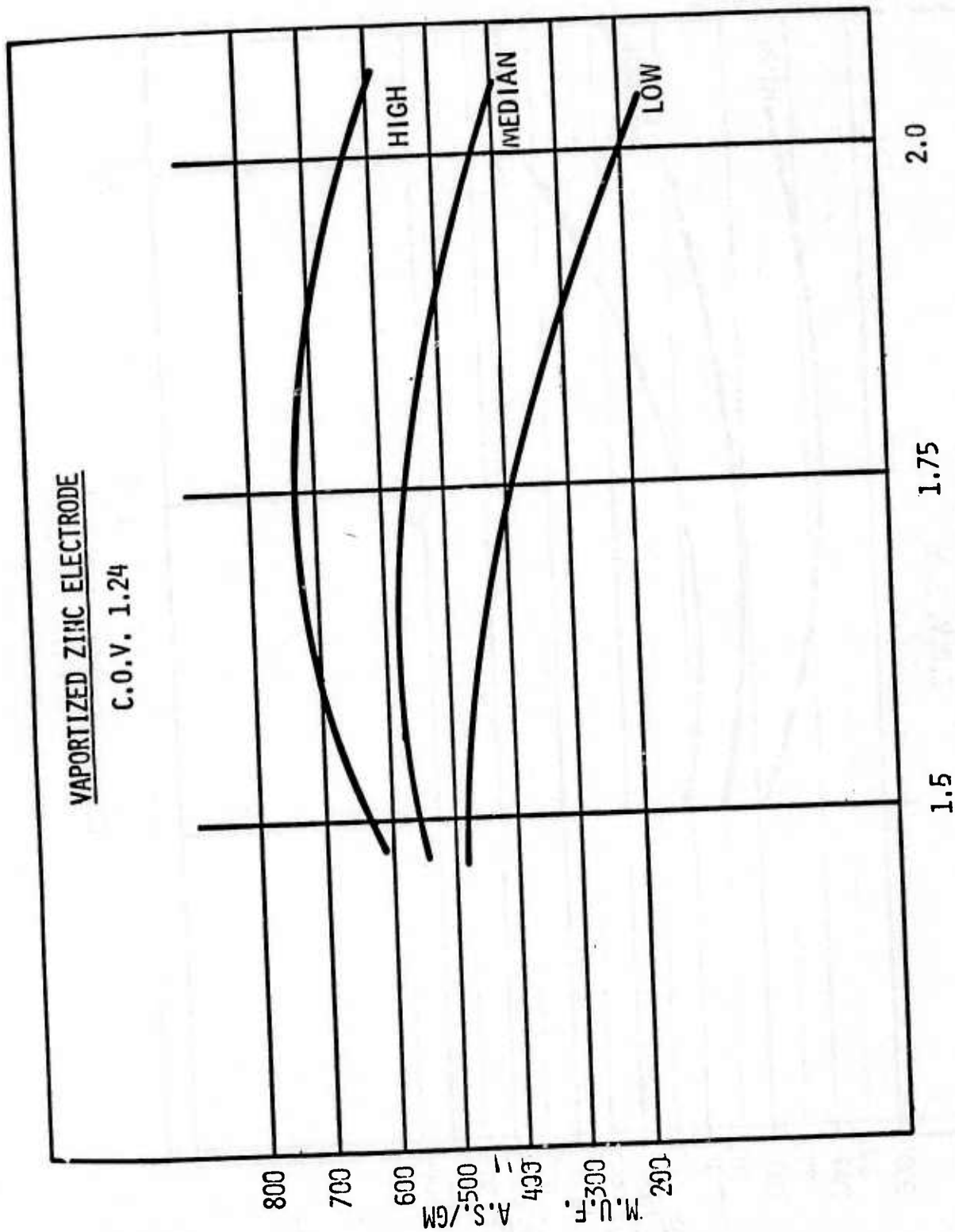


Figure 14 - Zinc Material Utilization Factor - 1.20C.O.V.



CURRENT DENSITY - AMPS/IN²

Figure 15 - Zinc Material Utilization Factor - 1.24 C.O.V.

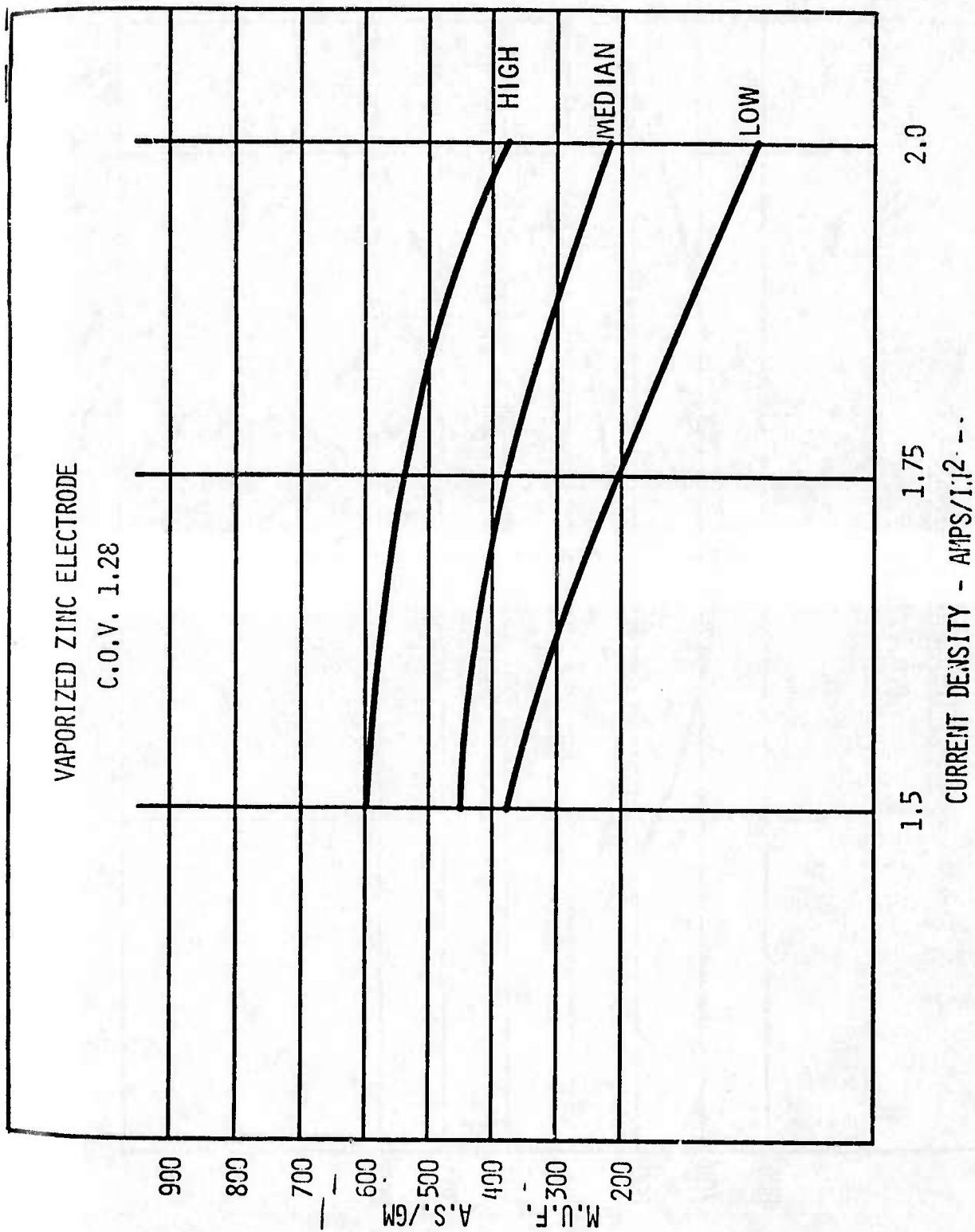


Figure 16 - Zinc Material Utilization Factor - 1.28 C.O.V.

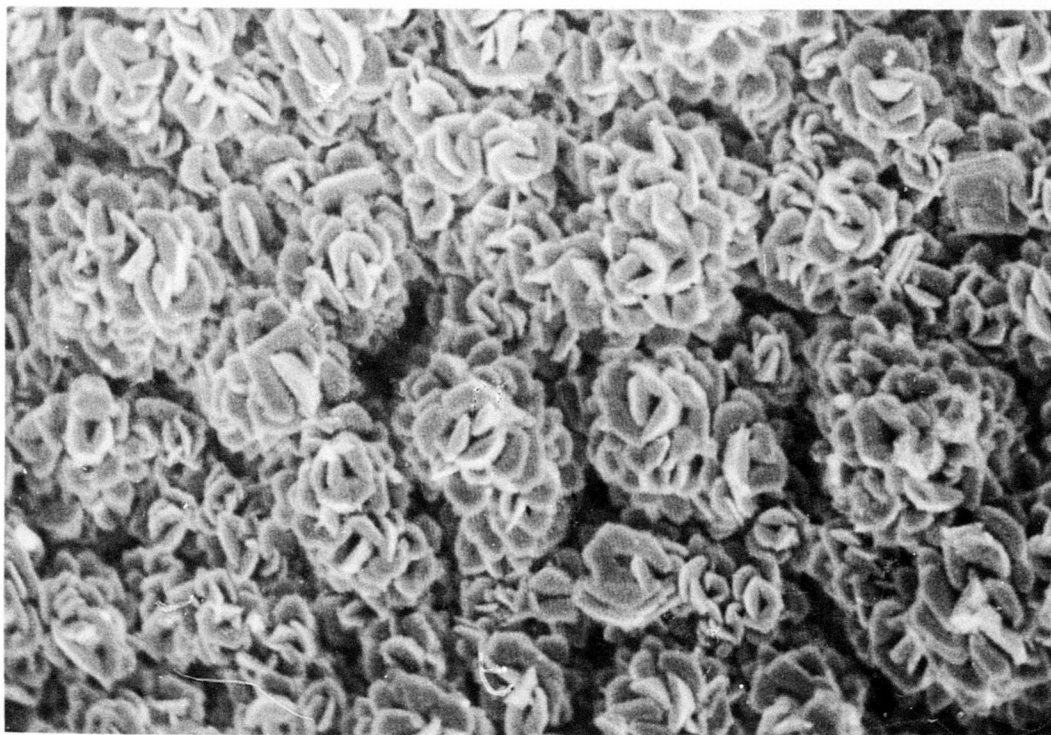


Figure 17 - Negative Electrode - 300X

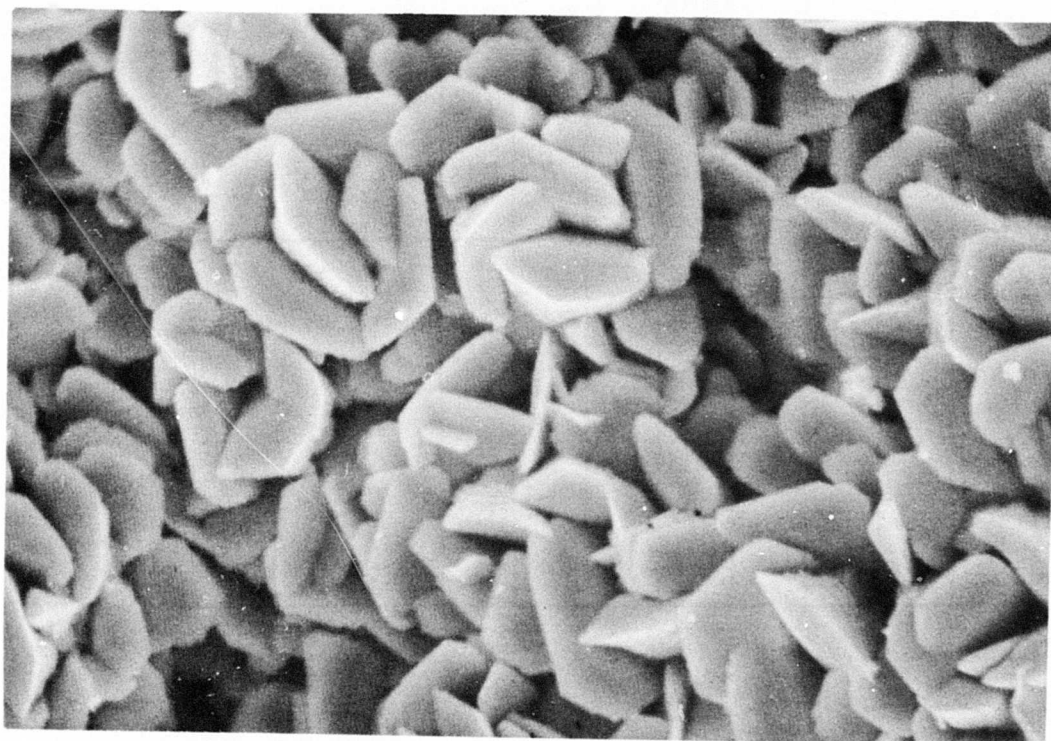


Figure 18 - Negative Electrode - 1000X

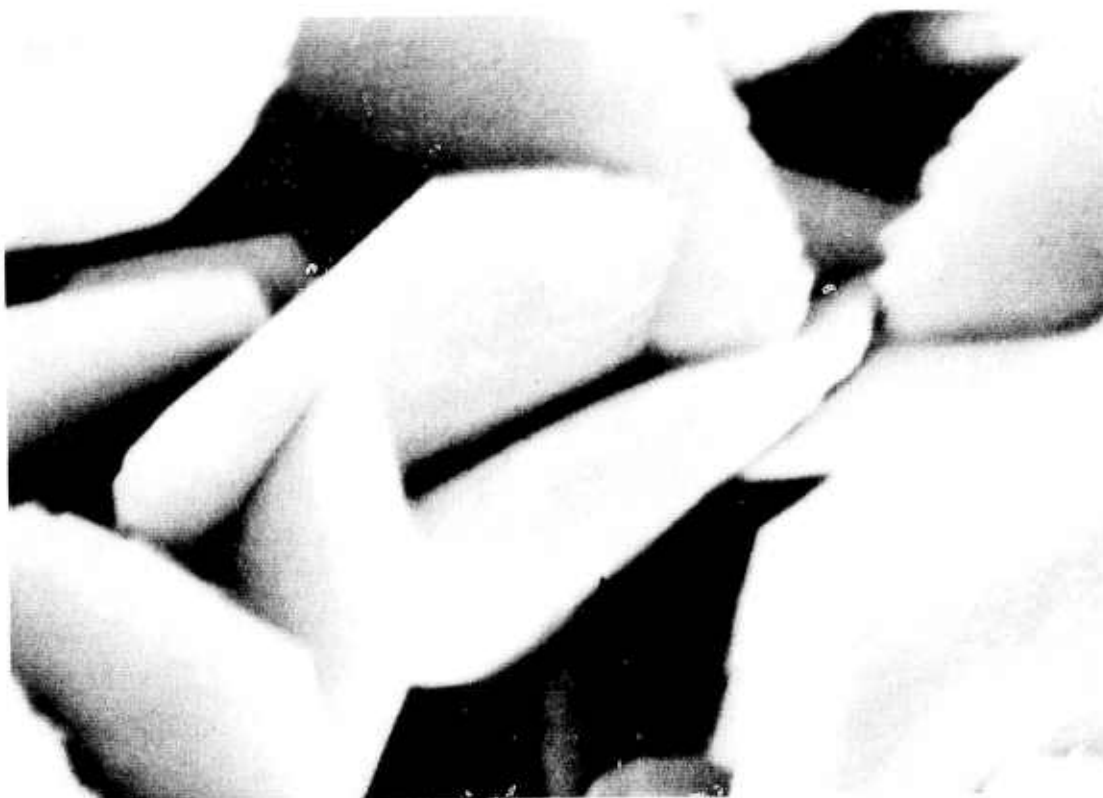


Figure 19 - Negative Electrode - 3000X

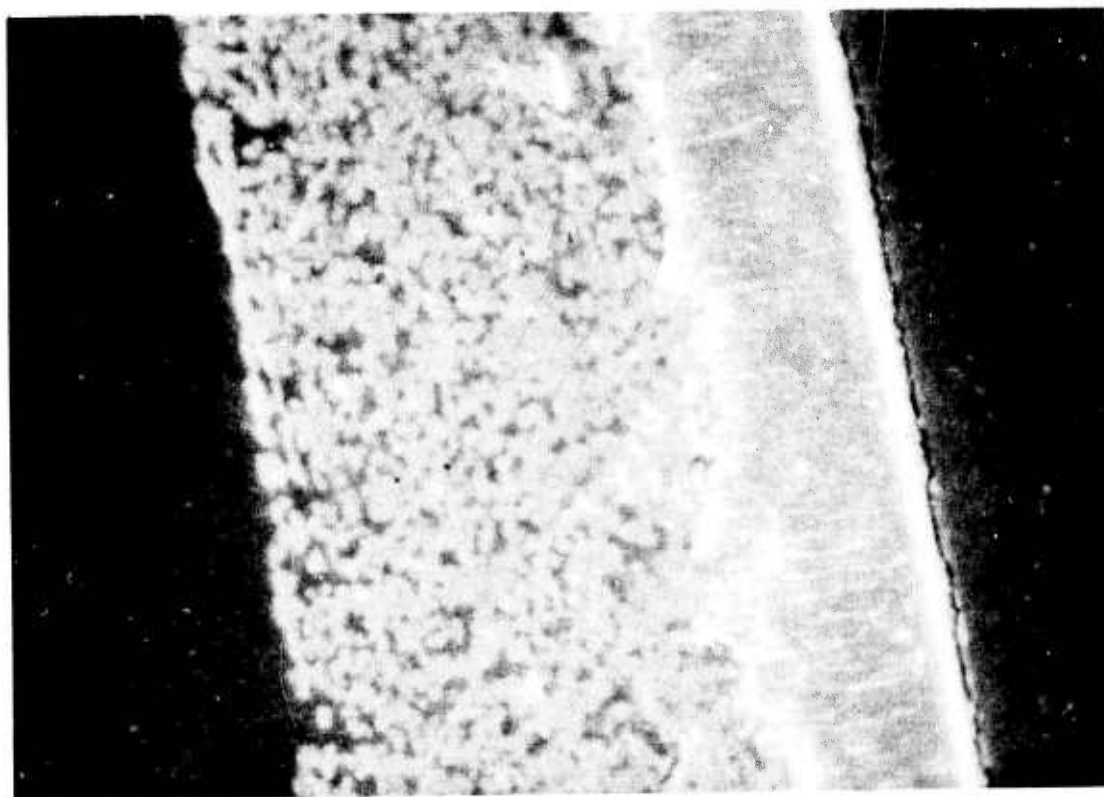


Figure 20 - Negative Electrode - Cross Section



Figure 21 - Negative Electrode - Cross Section - 3000X

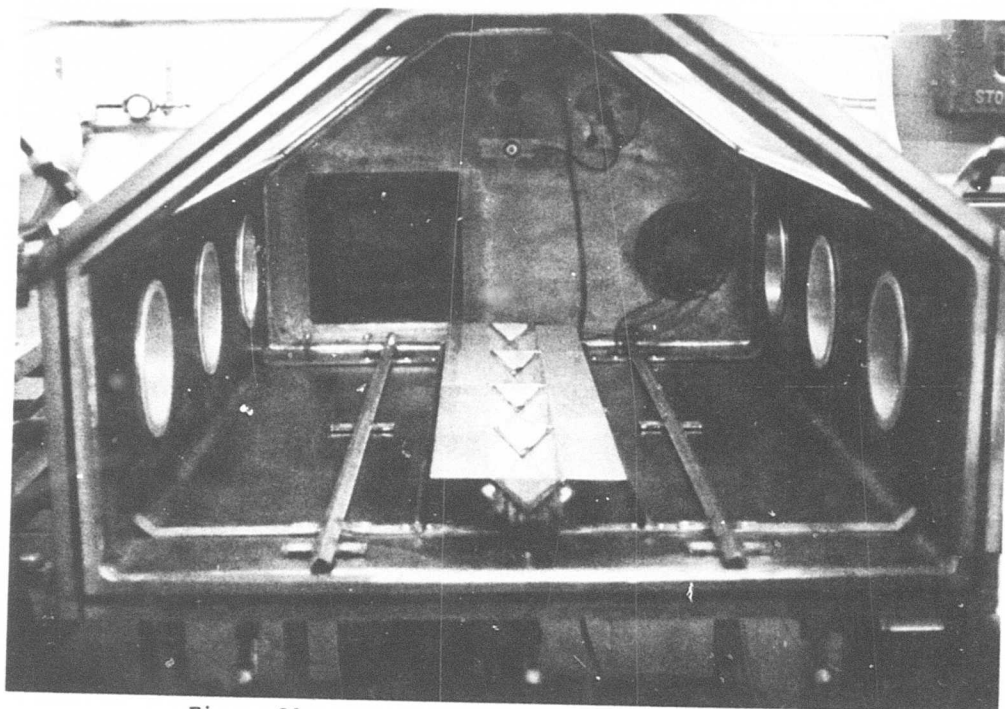


Figure 23 - Negative Electrode - Deposition Chamber

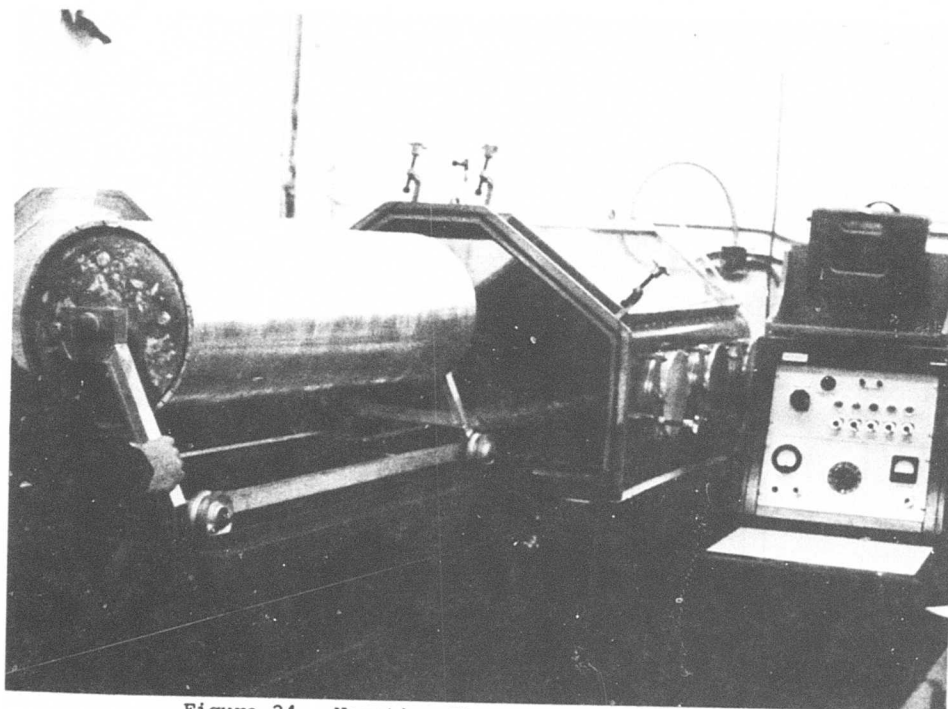


Figure 24 - Negative Electrode - Substrate Drum

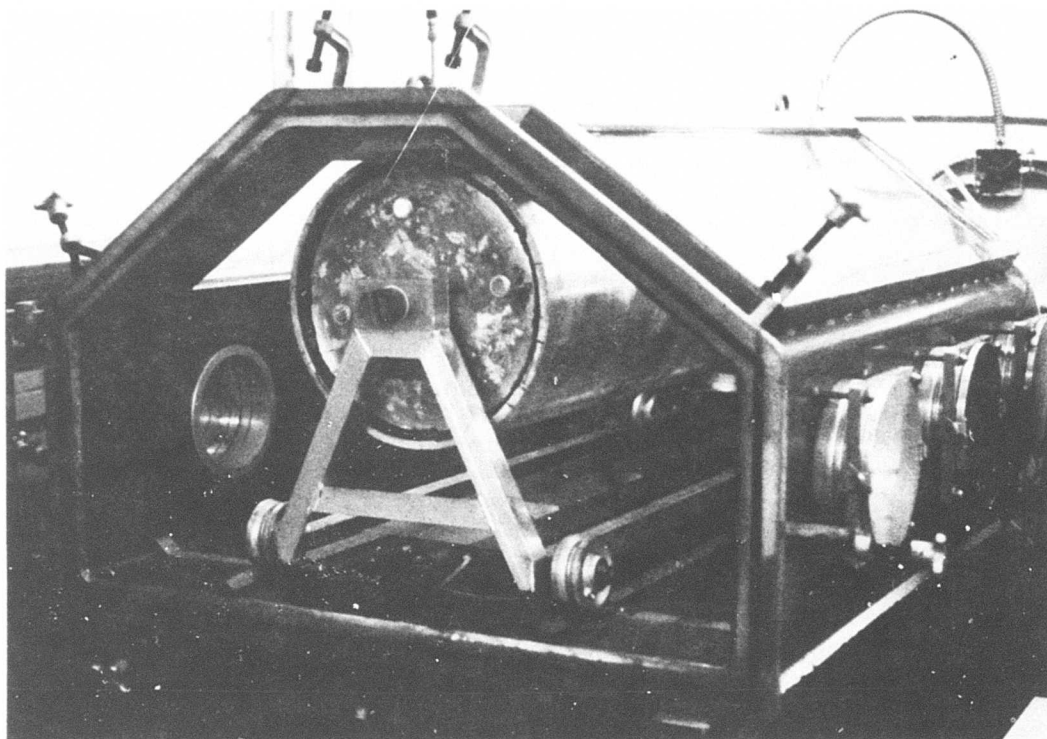


Figure 25 - Negative Electrode - Drum and Chamber

3.3 Separator

The separator system as used in the silver zinc battery is essential in retaining the active materials in the immediate vicinity of their respective electrodes. It is also used in retaining electrolyte in the cell compartment and for impeding diffusion of the soluble silver. Other important characteristics are weight and volume consistent with minimal electrical and chemical resistance.

Studies were directed during this contract toward determining, from potential separator candidates, a complete system to effect the above characteristics. The separator system has been evaluated considering three (3) distinct elements; namely, positive absorbant, barrier and negative absorbant. Each absorbant serves as an electrolyte reservoir as well as a protective shield of active materials from the barrier. This is especially necessary at the positive electrode due to the highly oxidizing nature of silver oxide. The barrier separator serves as a semi-permeable sieve for impeding silver migration to the negative electrode.

3.3.1 Component Development

At the beginning of this contract, two (2) potential separator candidates were available for a barrier material. They were Cellophane and Permion. In order that an immediate evaluation could be initiated, a stand and cycle test program was started. Ninety (90) conventional silver zinc cells were assembled using various combinations and grades of Cellophane and Permion for the barrier separator. Absorbent separators were mainly restricted to Webril and Pellon. A summary of cells which performed a minimum of thirty (30) cycles is shown by Table II. The cells were constructed in a conventional manner using the separator system shown and discharged at a current

density of 1.5 amps per square inch. Basically, the data shows the Permion capability to be in the range of 30 to 35 cycles while Cellophane is from 40 to 50. The major failure mode in these cells was from the zinc "shape change" and not attributable to the particular separator system. However, the Permion separated cells did appear to promote "shape change" resulting in earlier failures. A comparison is also made in Table II as to the voltage losses calculated vs. actual during the test. The results are quite predictable substantiating our resistance measurements taken in previous tests. The physical characteristics of each barrier separator is also shown in this figure, which is considered on its weight and volume contributions to module/systems projections.

From the above tests, the two (2) most promising separator systems overall were three (3) layers, one (1) Cellophane (PUDO 193) and one (1) layer of Permion E-2193-40/20. These materials were utilized in fabrication of piles for a designed test matrix. Typical performance data is shown in discharge curves of Figure 26 at the twentieth charge/discharge cycles.

At this time the three (3) layers of Cellophane (PUDO 193) was adopted as the standard barrier separator. The absorbent materials were M1405 Webril on the positive and 2504 Pellon on the negative electrode. Later in the contract, the negative separator was changed to R-25D Viskon due to procurement problems. The Viskon has performed equally as well and possibly better since it acts as a sacrificial material to silver, which has migrated through the barrier.

3.3.2 Components Configuration

Figure 27 shows the physical configuration of the complete separator/seal, which is presently being used in pile construction and testing.

Each absorbent piece is precut and heat sealed to the other to form an envelope. The barrier material (cellophane) is folded to dimension and inserted into the envelope.

The three (3) separator components are, from positive to negative electrode, M1405 Webril (one (1) layer), Cellophane (three (3) layers) and R25D Viscon (one (1) layer). The M1405 Webril is fabricated from Dynel fibers into a non-woven mat .001 inch thick. When wetted with electrolyte, it retains its original thickness. The Cellophane, designated PUDO 193, is cellulosic in origin and processed to a dry thickness of .0015 inch and surface area of 19,300 inch²/pound. The wetted thickness doubles increasing to .003 inch. R-25D Viscon is also a non-woven material and is fabricated from Nylon (Polyamide) fibers. They dry thickness is .0025 inch and increases to .004 when wet with electrolyte. Combining all three (3) separators produces a package .014 inch thick.

3.3.1 Processing

Processing of the separator package is discussed in detail in Paragraph 4.1 and consists of the following steps:

1. Precut separator material.
2. Fabricate heat sealed absorbent envelope.

Prior to use in the pile assembly, the separator assembly is attached to the teflon seal also described in Paragraph 4.1 and shown in Figure 27.

TABLE II

CELL NO.	SEPARATION TYPE		THEO MV DROP	ACTUAL MV	NOM. VOLT 0-30 SEC	TOTAL CY COMPLETE	TOTAL DAYS STD	NO. LAYERS	DRY WT GM/IN ²	KOH WT GM/IN ²	TOT. TK. (IN.) WET
	POS.	BARRIER									
CYC STD					20 Cyc						
37	2504 K Pellon	3-PUDO 193	45	0	1.35	47	120	3	.023	.054	.009
38											
39											
43	Asbestos	3-PUDO 193	45	0	1.35	47	210	3	.023	.054	.009
44											
45											
52	1405 Webril	2-E2291 40/10 2504 K Pellon	75	60	1.29	49	90	2	.044	.065	.009
53											
54											
10	2504 K Pellon	3-E2291 40/20 1405 Webril	67.5	70	1.28	44	60	3	.021	.011	.0045
11											
12											
64	1405 Webril	1-E2192 40/20 1405 Webril	52.5	100	1.25	30	180	1	.066	.119	.007
65											
66											
76	1405 Webril	2-P2190 40/20 2504 K Pellon	90	100	1.25	35	180	2	.040	.065	.0074
77											
78											
70	1405 Webril	1-P2190 40/20 2504 K Pellon	45	40	1.31	35	90	1	.040	.065	.0037
71											
72											
79	1405 Webril	3-PUDO 193	45	0	1.35	40	120	3	.023	.054	.009
80											
81											
25	1405 Webril	2-E2190 40/20 2504 K Pellon	75	80	1.27	33	210	2	.040	.065	.0074
26											
27											

TABLE II
(Continued)

CELL NO.	CYC	STD	POS.	SEPARATION TYPE BARRIER	NEG.	THEO MV DROP	ACTUAL MV	NOM. VOLT 0-30 SEC	TOTAL CY COMPLETE	TOTAL DAYS STD	NO. LAYERS	DRY WT GM/IN ²	KOH WT GM/IN ²	TOT. TK. (IN.) WET
								20 Cyc						
22	19		2504 K	1-E2190 40/20	1405	37.5	40	1.31	32	120	1	.040	.065	.0035
23	20		Pellon		Webril									
24	21													
13	16		Asbestos	3-E2291 40/20	1405	67.5	50	1.30	33	30	3	.021	.011	.0045
14	17				Webril									
15	18													
34	31		1405	1-E2193 40/20	2504 K	60	60	1.29	30	210	1	.065	.076	.009
35	32		Webril		Pellon									
36	33													

CELL NO.	GM/IN ²	TK IN.	SEPARATOR	VOLTAGE COMPARISON
• 59A	.277	.006	3 PUDO	CYCLE 20
X 87	.24	.006	1-E2193 40/20 2 (40/20) 1 CELLO	

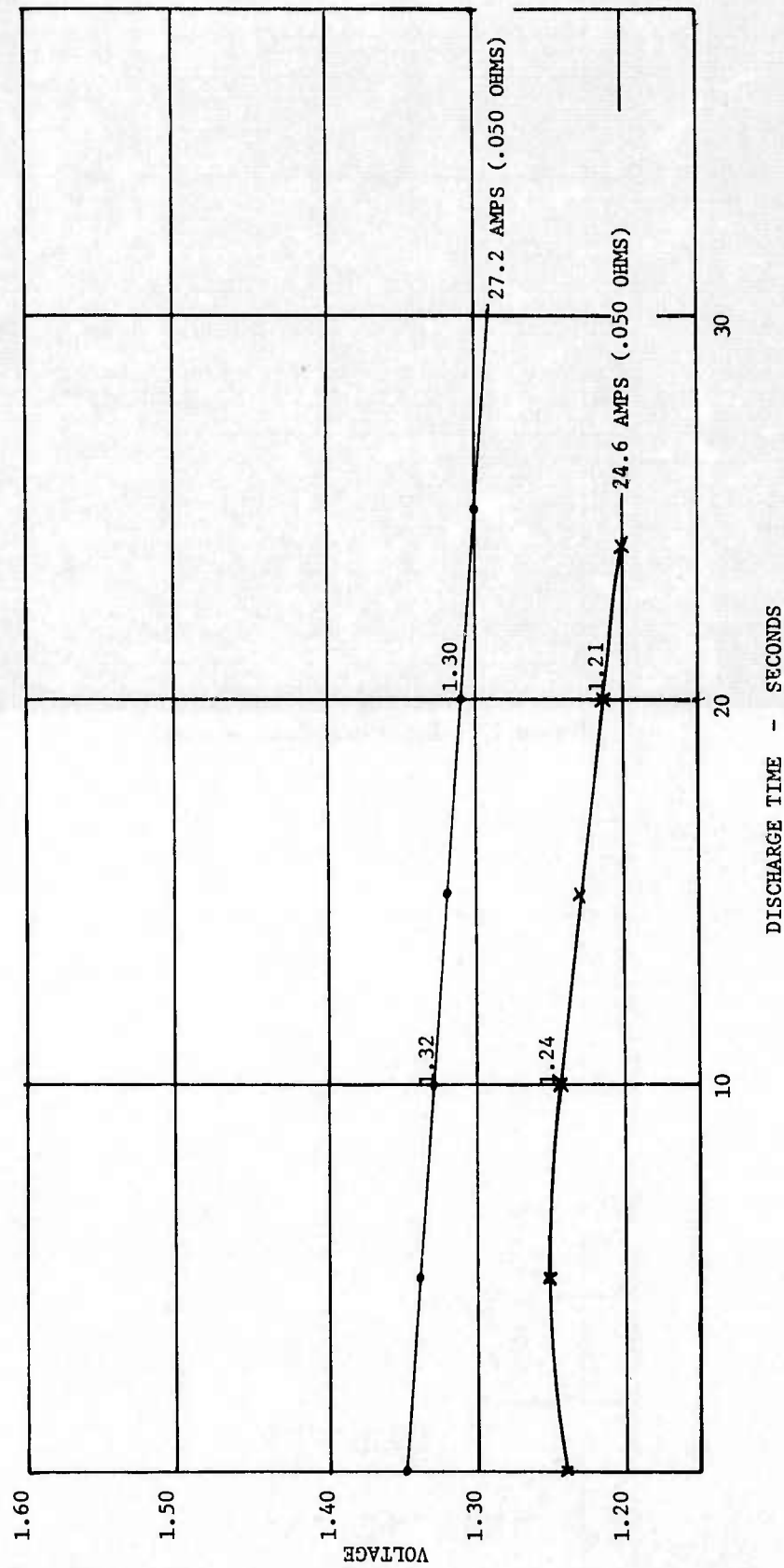


Figure 26 - Separator Effects on Cell Voltage

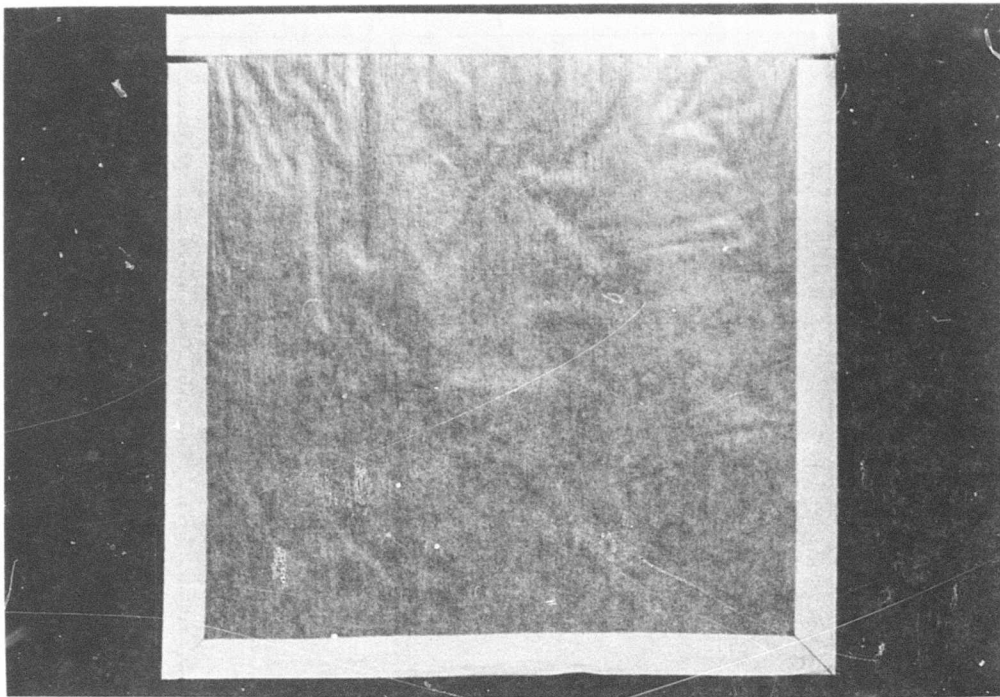


Figure 27 - Separator/Seal Assembly

3.4 Seal/Adhesive

In the fabrication of pile type batteries, it becomes necessary to electrically isolate the individual electrodes and form a cavity for retention of the electrolyte. Therefore, the seal is utilized to serve both purposes. In the present design, an epoxy adhesive is used to position and retain a teflon seal in its proper location.

3.4.1 Component Development

Development of a seal/adhesive which would withstand the physical, chemical, and electrical requirements for the subject design has been limited mainly to two (2) types. They are: (1) teflon with epoxy adhesive and (2) molded rubber.

The majority of actual test piles constructed used the Teflon - epoxy seal arrangement. However, several rubber seals were built and tested. The rubber was compounded by the Materials Laboratory at Wright Patterson Air Force Base and integrated into a test matrix conducted by Eagle Picher. The test matrix consisted of twelve (12) combinations of basic compounds, cure times and adhesives. The results of all these tests were considered to be equal to that of teflon. The positive side of the electrode was well adhered while the negative side separated. The separation usually occurred between the adhesive and the silver foil and is attributed to corrosion problems associated with the negative electrode.

In order that an effective seal may be obtained, to conduct pile tests, it is only necessary that one side of the bipolar electrode be sealed. The resulting design included extension of the seal material beyond the silver foil by approximately .060 inch. With a seal on the positive side and an epoxy coating on the extended teflon, individual cell compartments are formed.

Processing of the Teflon seal is more flexible and easily produced at Eagle Picher than the molded rubber. Therefore, it has been established as the basic seal design. Numerous test cells and piles have been fabricated (approximately 250) during this contract period with no degradation experienced in the use of Teflon.

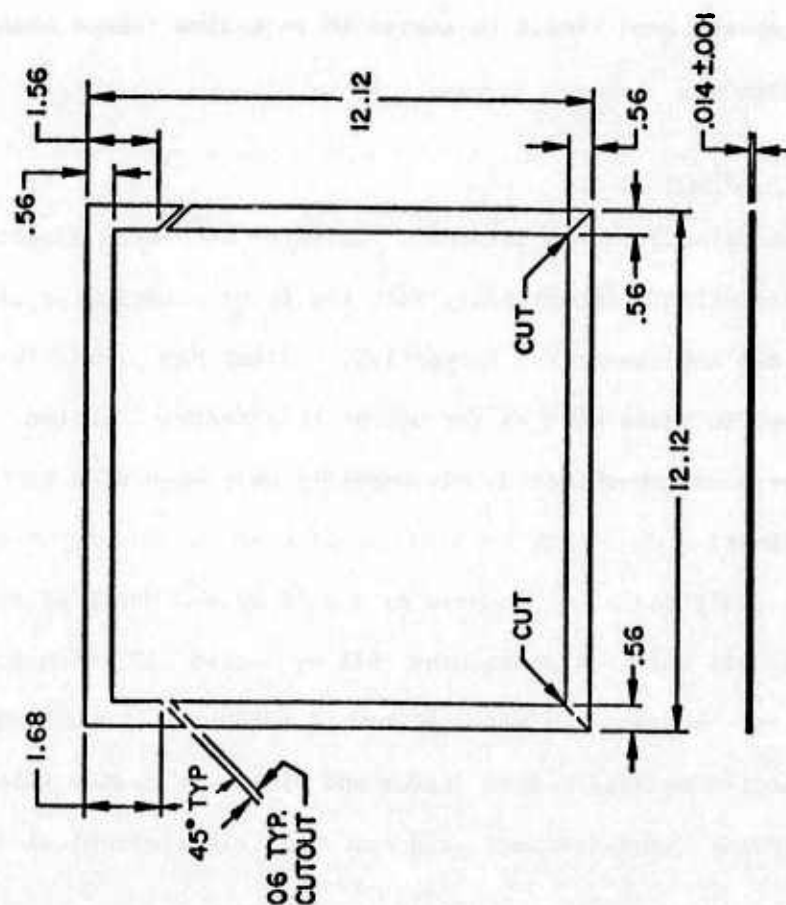
3.4.2 Component Configuration

The seal/adhesive system used in the present pile battery design consists of unsintered Teflon and two (2) part epoxy. Paragraph 4.1 describes a physical description of the seal/adhesive in combination with the separator to which it is assembled.

The Teflon film is processed from virgin TFE resin at Eagle Picher. It forms a porous matrix sheet and is used in the unsintered condition from which strips are cut via steel rule dies according to the dimensions shown by Figure 28. The porous matrix provides adequate surface area, so that the adhesive may penetrate post the surface effecting a good mechanical bond. The unsintered condition provides compression flow allowing the seal to conform readily to its confines.

The adhesive used to position and retain the seal is manufactured by the HB Fuller Company and designated as Fuller Resiweld FE7004.

Assembly of the seal is accomplished by positioning the precut Teflon around the perimeter of the separation package as shown previously in Figure 27.



NOTES:
 1. MATERIAL: POUROUS UNSINTERED TEFLON
 BLEND PER E-P PROPRIETARY PROCESS
 USING DUPONT TYPE 6C FLUOROCARBON
 RESIN.

Figure 28 - Seal Configuration

3.5 Intercell Connectors

The intercell connector for the subject battery design serves as the cell case, active material substrate, as well as the series connection between individual cells for electrical continuity. It occupies approximately ten (10) percent of the projected module volume and is approximately forty (40) percent of the total weight. In addition to volume and weight, the electrical resistance and corrosion resistance must also be maintained at minimal levels.

The intercell connector of the pile design minimizes the electrical path from cell-to-cell to .001 to .002 inches, resulting in a considerable reduction in voltage losses. Since the connector serves as a common substrate to both active materials, the current is distributed evenly across its surface, which should lend itself to assist in retarding "shape change" of the negative electrode.

3.5.1 Component Evaluation

Studies pertaining to the intercell connector have been directed toward; surface preparation, compatibility with the electrochemical system, and overall mechanical and electrical properties. Silver has primarily been the material utilized in these studies throughout this contract period. Other materials have been investigated, but normally only when used in combination with silver.

The silver foil has been procured as a cold rolled strip of fine quality per MIL-S-13282A and in a continuous roll by twelve (12) inches wide. Preparation of the foil surface was directed toward producing a rough surface for attaching the active materials, both silver and zinc. Processes which were evaluated included: sandblasting, acid etch, and electrochemical etch.

A series of tests were conducted for these three (3) processed to determine contact time, solution strength and current density as applicable. Results of these studies were compared by physical examination and SEM photographs. Figures 29, 30 and 31 show typical surface condition after treatment by the three (3) processes. Foil which has been sandblasted results in a desirable surface; however, since the silver is malleable, wrinkling and distortion occurs disrupting the desired flatness for subsequent processing. The electrochemical etch in potassium cyanide produces a "cratered" surface with increased surface area as compared to the other methods.

Figure 32 is a SEM photograph of "as received" silver foil. Samples were scanned for holes, pits, etc., which could produce problems in an active cell. The largest imperfections found are typical of the pit shown, being approximately five (5) micron across and is only a surface defect not penetrating through the foil.

Other materials which have been evaluated include: titanium, zinc and copper foil. The titanium possessed good weight projection by reducing a four (4) megawatt system by .470 pounds. However, due to passivation of titanium and incapability with processing the sintered silver material, it was designated as an unacceptable candidate.

In the studies of the negative electrode (Reference Paragraph 3.2) it was found desirable to protect the silver foil on the negative side from the common electrolyte. To achieve this approach, both copper and zinc were considered. Zinc, when used as a direct replacement for one half of the intercell connector, would result in 120 pounds. In considering zinc and copper, test cells were constructed and tested. No electrical performance degradation was observed in the use of either. The zinc seal was improved in reference to sealing to the negative side which indicates less

corrosion occurs. Copper does not show any improvement by itself, but would be an acceptable interface as a strike between zinc and silver foil. Pin holes in the zinc foil could result in corrosion with the silver foil requiring a continuous deposition. The intermediate copper strike could provide an electrolyte barrier. Actual test data has not been accumulated to date supporting this design, but it is of immediate interest to improve the intercell connector in conjunction with the negative electrode.

3.5.2 Configuration

The present design consists of an electrochemical etch of silver foil in potassium cyanide of the final bipolar electrode dimensions. The initial foil material is etched according to Paragraph 3.5.3 and results in a final thickness of approximately .0018 inch thick.

3.5.3 Processing

Processing the silver intercell connector is accomplished by the following steps starting with .002 inch thick cold rolled foil which has passed acceptance by receiving and inspection:

1. Foil which has been accepted for use in bipolar plate construction is cut into 12 x 13 inch sheets.
2. Each sheet is annealed at 600°C for two (2) minutes.

NOTE: FROM THIS POINT ON, THE OPERATOR SHALL WEAR WHITE COTTON GLOVES, OR EQUIVALENT, WHEN HANDLING SILVER FOIL SHEETS. STORAGE SHALL BE ON CLEAN TRAYS WITH SUITABLE COVERINGS TO PREVENT CONTAMINATION.

3. Each sheet is connected by one of the 13 inch sides to bus bar allowing a complete 12 x 12 inch surface to be exposed, in a plating tank, to a potassium cyanide solution, (95 \pm 5 grams of potassium cyanide per liter of water).
4. The foil shall be made anodic with reference to a nickel cathode for 1.5 minutes at a rate of 55 \pm 3 amperes per square foot.

5. Each sheet shall be removed from the cyanide tank and spray rinsed for 2 minutes in running tap water.
6. The plates shall then be placed in storage containers until time for the porous silver deposition.
7. Prior to the porous silver deposition, each sheet shall be cut to its final size and step 2 repeated.
8. Weigh each piece of silver foil and record weight on one corner of plate.

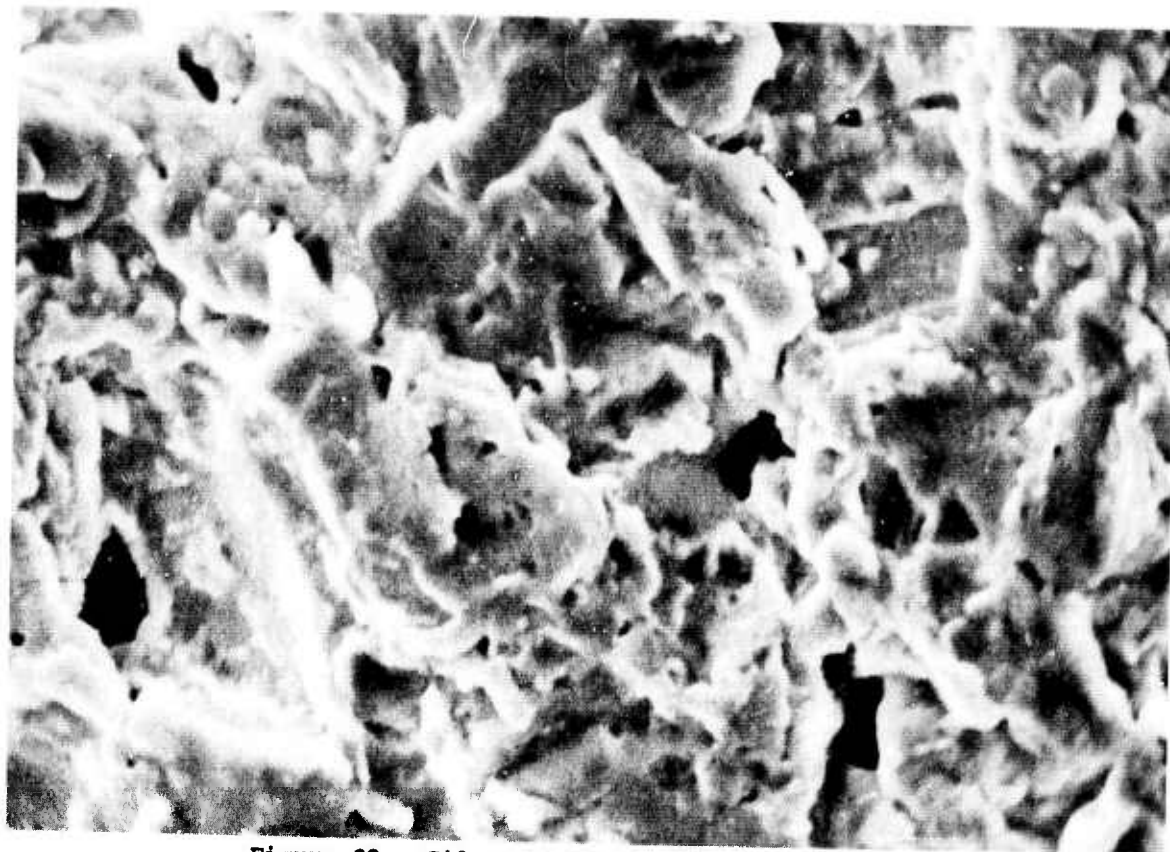


Figure 29 - Silver Foil, Sandblasted - 1000X

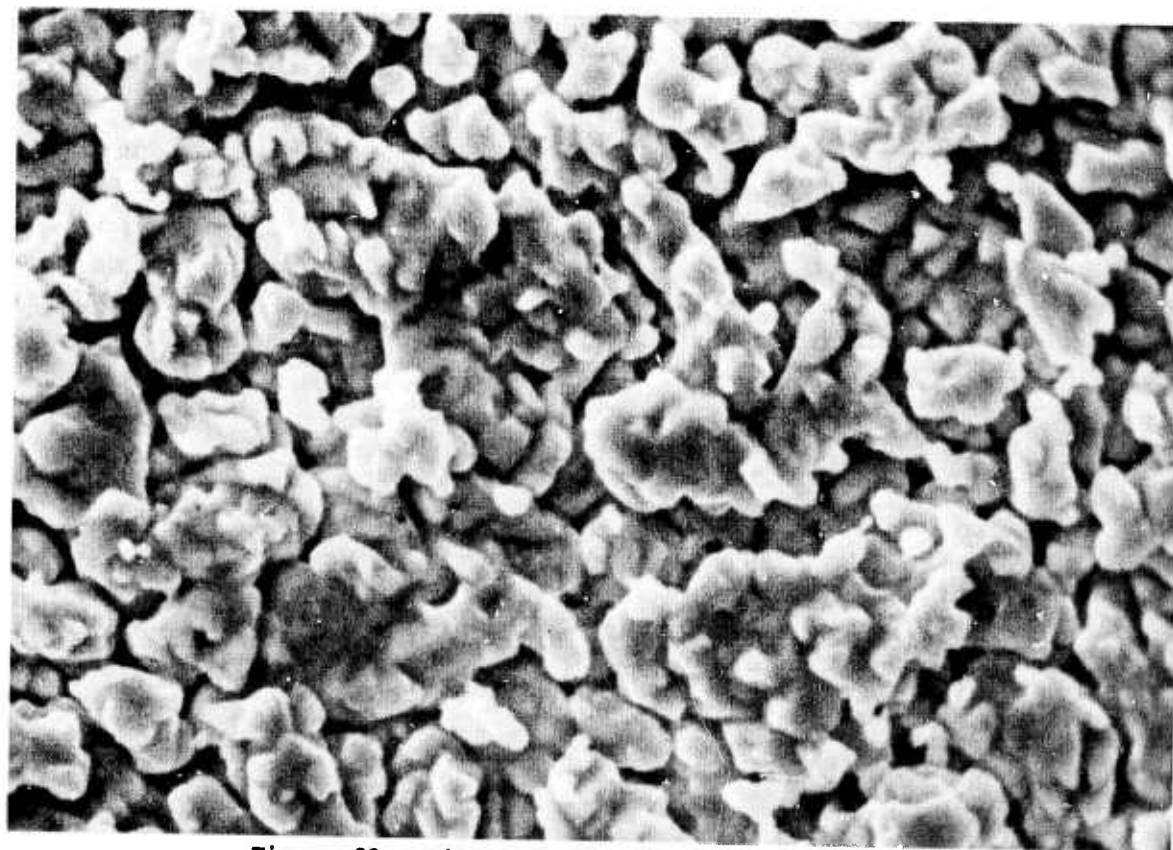


Figure 30 - Silver Foil, Acid Etched - 1000X

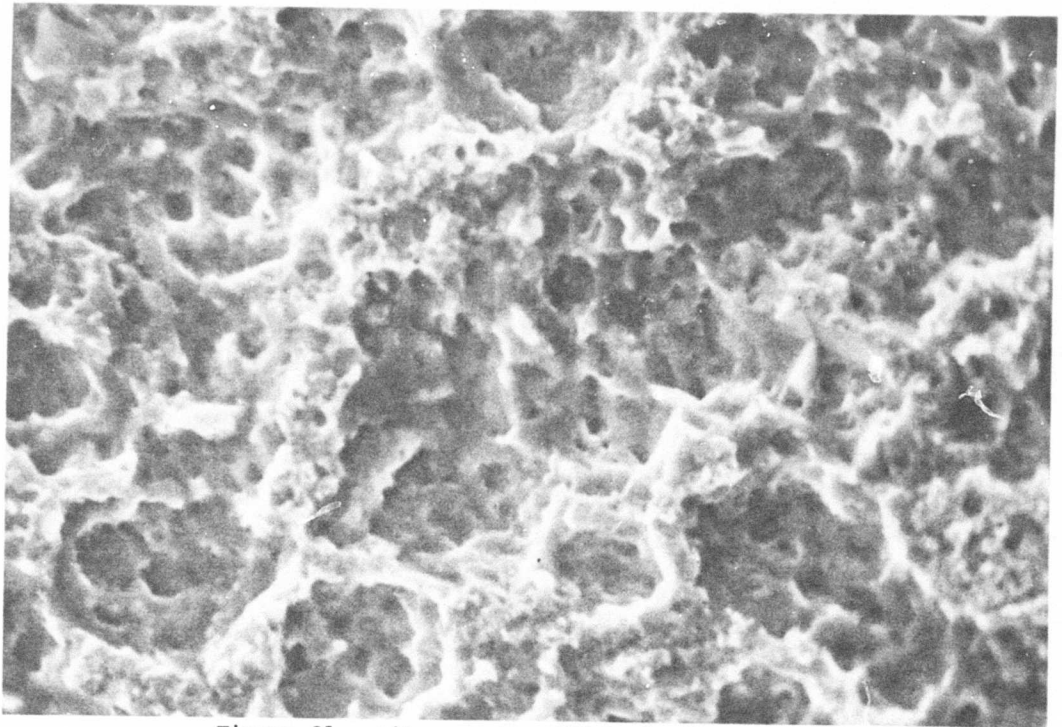


Figure 31 - Silver Foil, KCN Deplating - 1000X



Figure 32 - Silver Foil as Received - 1000X

4.0 Test Article Configuration and Fabrication

Design configuration and fabrication techniques for single and multi-cell piles are adaptations of processing procedures and drawings which have been established for full scale submodules. Using this approach allows for verification and/or modification to the drawings and written procedures while maintaining fixed guidelines for test cell fabrication. At the present time, the general steps involved in the construction of a test cell are outlined on the Flow Chart in Figure 33.

4.1 Electrode Fabrication

The preparation of electrodes has been previously explained in Paragraphs 3.1 and 3.2.

4.2 Separator-Seal Sub-Assembly

The Teflon utilized for the seal is a porous unsintered Teflon manufactured from Dupont Fluorocarbon Resin and is rolled into a sheet stock of the desired thickness in large batches and stored. The separator is comprised of three materials;

1. M1405 Webril
2. R25D Viskon
3. Pudo 193 Cellophane

and, is precut and folded according to Figure 34. The following steps are the written process procedures for assembling the separator-seal sub-assembly:

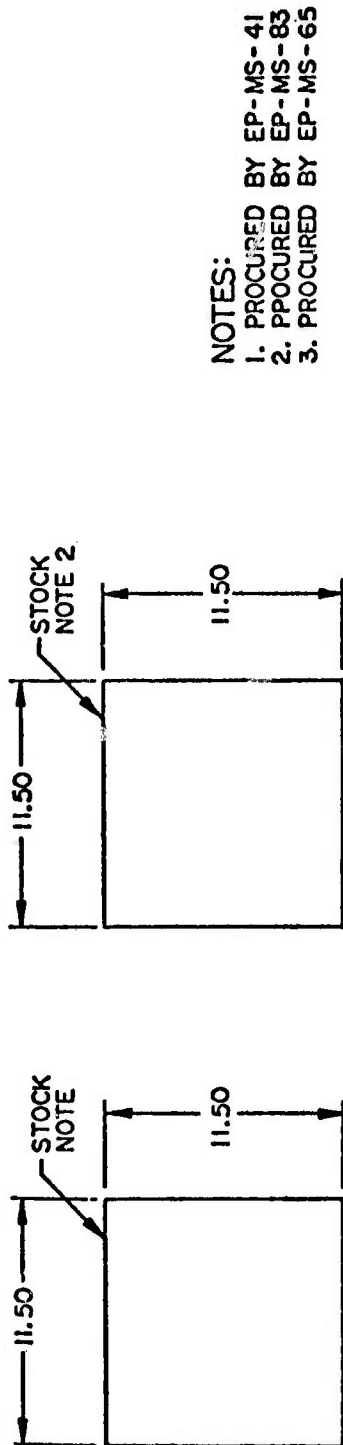
1. Fold precut cellophane to make a 3 layer separator package 11.18" x 11.25".
2. Using steel rule die per Figure 28 and a pressure setting of 500 psig, punch teflon strips using blotter paper between teflon and upper press platen.
3. Separate teflon strips into top, bottom, short side and long side stacks.

4. Using the heat sealing fixture, heat seal two (2) edges of the 11.5" x 11.5" R25D Viskon to the 11.5" x 11.5" M1405 Webril.
5. Insert prefolded cellophane separator, open edge up, between the R25D Viskon and M1405 Webril.
6. Using the heat sealing fixture, seal the third edge of the R25D Viskon to the M1405 Webril.
7. Finish and stack all separator packages prior to proceeding.
8. Using the adhesive applicator, apply a 1/2 inch wide edge of adhesive to the separator package on the R25D Viskon side.
9. Place the separator package in the assembly fixture.
10. Place teflon strips in fixture starting with the long side on the right.
11. Place polyethylene film over the separator seal assembly.
12. Repeat steps 5 through 11, alternating the long side teflon strip from right to left, until all seal/separator subassemblies are completed.
13. Place aluminum sheet on top of seal/separator subassemblies and press to 5 psi and allow adhesive to cure for twelve (12) hours.

The drawings in Figure 28 and Figure 35 show the physical configuration of the seal and the separator-seal assembly, respectively.

4.3 Vents

Vent tubes are presently manufactured from 0.046 inch O.D. shrink tubing. A 0.010 inch diameter stainless steel wire is inserted into a 6 inch long piece of tubing. Two (2) to three (3) inches of the tubing is then shrank around the stainless wire. The wire is left in place until all construction is completed and then removed leaving a 0.010 inch diameter hole through to the seal area and into each cell.



NOTES:
 1. PROCURED BY EP-MS-41
 2. PROCURED BY EP-MS-83
 3. PROCURED BY EP-MS-65

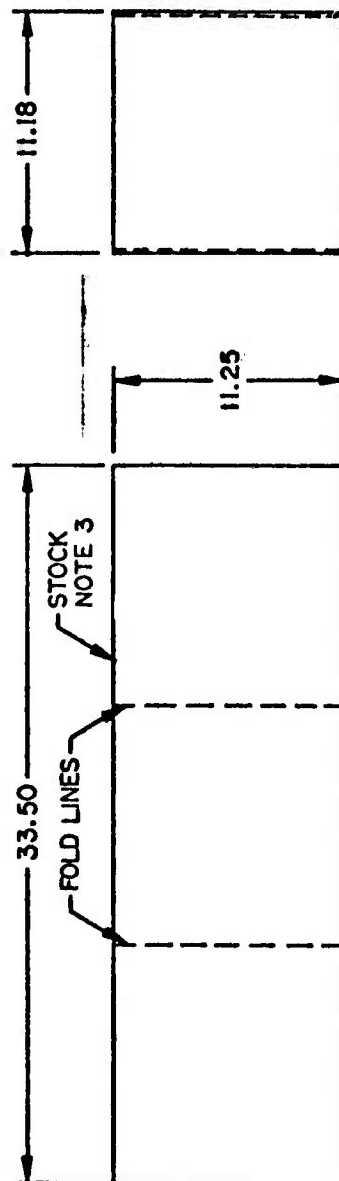


Figure 34 - Separator Configuration

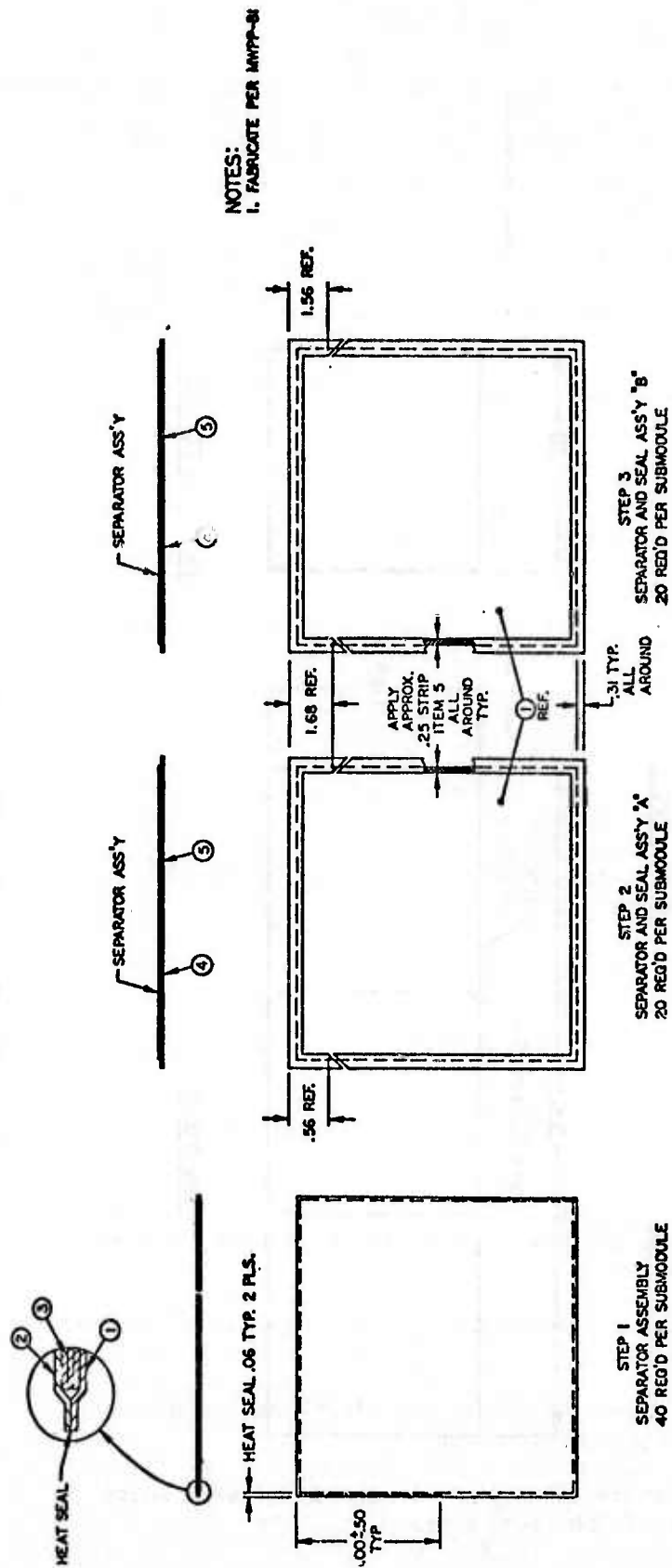


Figure 35 - Separator/Seal Subassembly

4.4 Cell Stack Assembly

Upon the completion and collection of all of the individual components, the assembly fixture is prepared as shown in Figure 36. A closed photograph of the fixture is shown in Figure 37. The following steps are taken to assemble the cell stack:

1. Set shims on the assembly fixture to required cell stack thickness (one to forty cells).
2. Install vent tube inserts.
3. Spray inside of fixture with Surfack mold release.
4. Apply a 1/2 inch wide layer of adhesive to the 4 edges of the positive end electrode and place it in the bottom of the fixture.
5. Position a vent tube in the left hand side of the fixture and against the positive electrode.
6. Apply adhesive to the separator side of the separator seal sub-assembly.
7. Position the separator seal sub-assembly in the fixture, separator facing down.
8. Position a vent tube on the right hand side of the fixture against the separator.
9. Apply adhesive to the separator seal sub-assembly in the fixture.
10. Apply adhesive to the negative side of a bipolar electrode.
11. Place the bipolar electrode in the fixture, negative side down.
12. Apply a 1/2 inch wide layer of adhesive to the four edges of the positive side of the bipolar electrode in the fixture.
13. Repeat steps 5 through 12 until all bipolar electrodes are installed.
14. Apply adhesive to negative end electrode and place in fixture, negative side down.
15. Lay the fixture cover plate in place. Insert bolts and tighten to physical stops.

16. Place the fixture in a vacuum chamber with 15 inches of Hg, and allow the cell stack to cure for 12 hours minimum.
17. Remove the fixture from the vacuum chamber.
18. Remove the fixture cover plate.
19. Remove the cell stack from the fixture.
20. Remove the wire inserts in all vent tubes.
21. Check for cell shorts by applying 100 volts DC from tab to tab and measure cell resistance.
22. Attach the sumps using adhesive (see Figure 38) and apply thin layer of adhesive to all 4 edges of the cell stack.
23. Allow the cell stack to cure for a minimum of 12 hours.
24. Clean positive and negative end electrodes with suitable solvent.

Figure 39 is the submodule assembly drawing and Figure 40 is a photograph of a completed full scale ten (10) cell pile. Variations in the photograph from the drawing are accountable, primarily, to the fact that test pile dimensions differ from the final submodule design.

4.5 Single Cell Configuration and Fabrication

Figure 41 is a photograph showing an exploded view of a full scale single cell. Only two (2) variations in the above configuration are required to build single cells. The first is the elimination of steps 10 to 13 in the cell stack assembly procedure in Section 4.4. The second is the use of remotely positioned sumps due to the lack of space available to attach a sump to the cell.

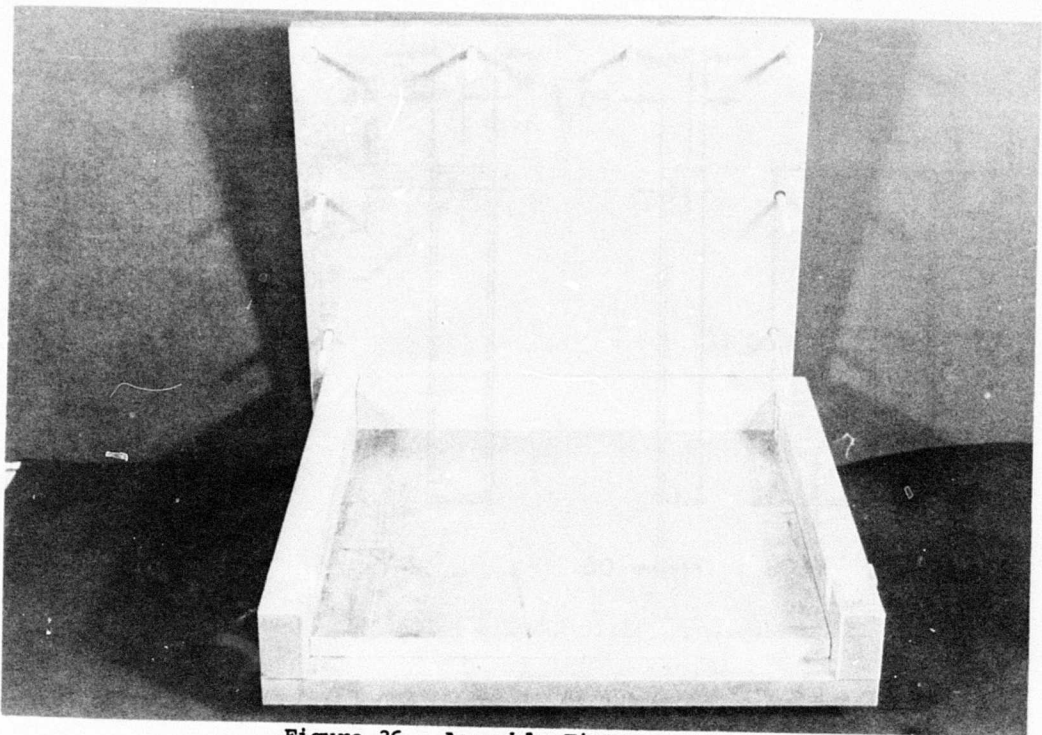


Figure 36 - Assembly Fixture - Open

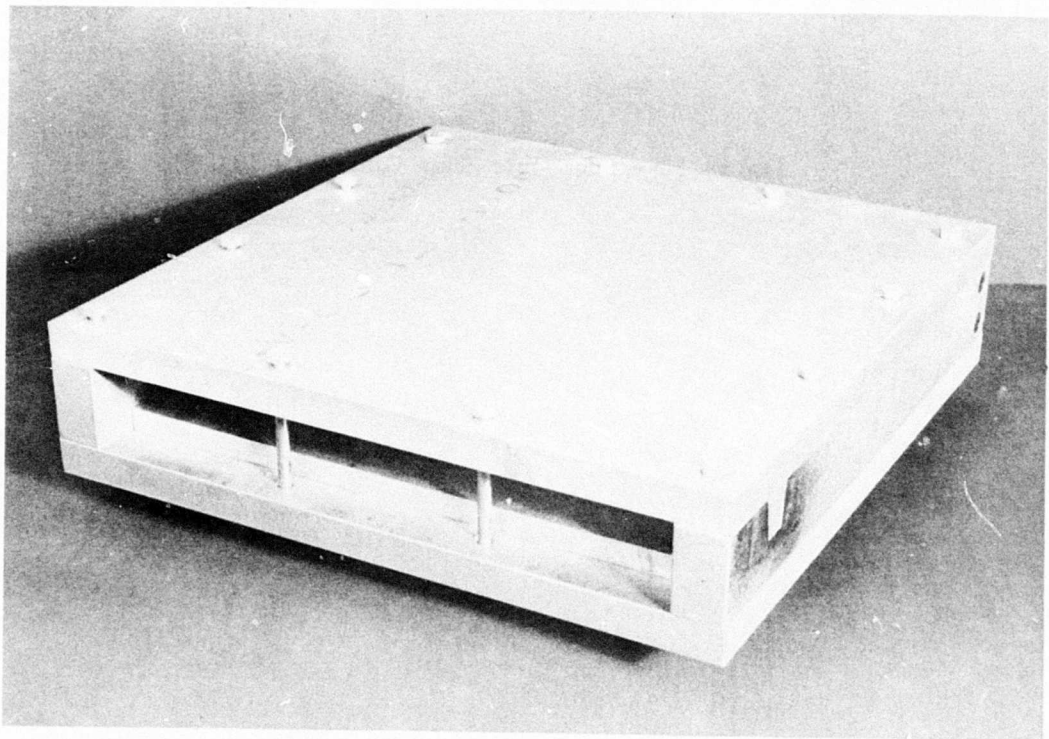


Figure 37 - Assembly Fixture - Closed

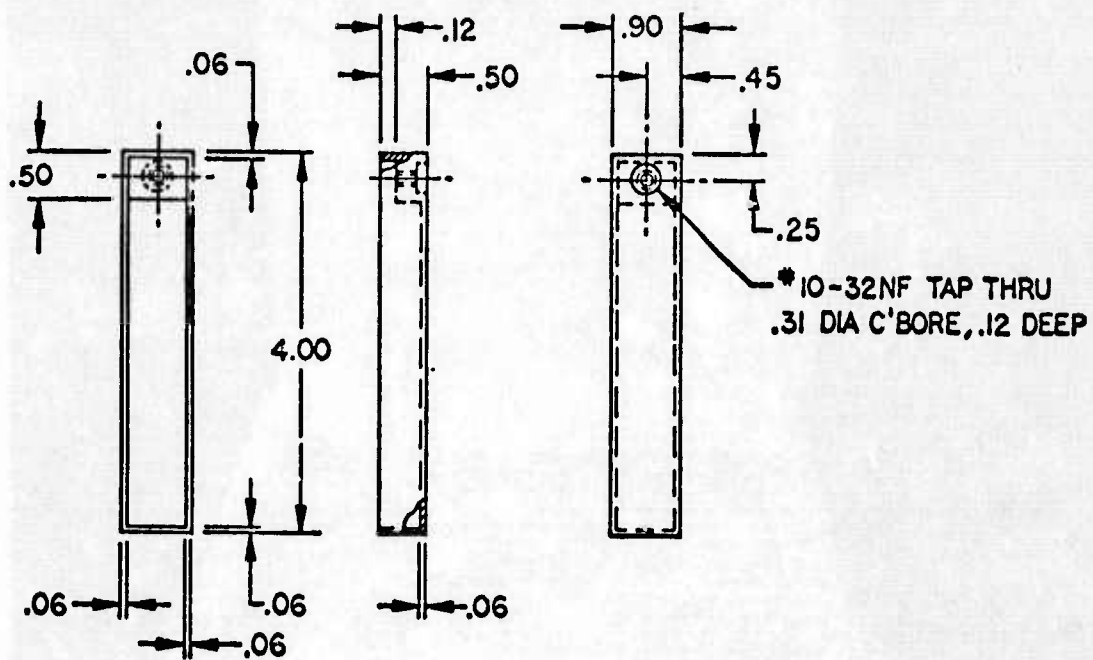


Figure 38 - Submodule Sump Configuration

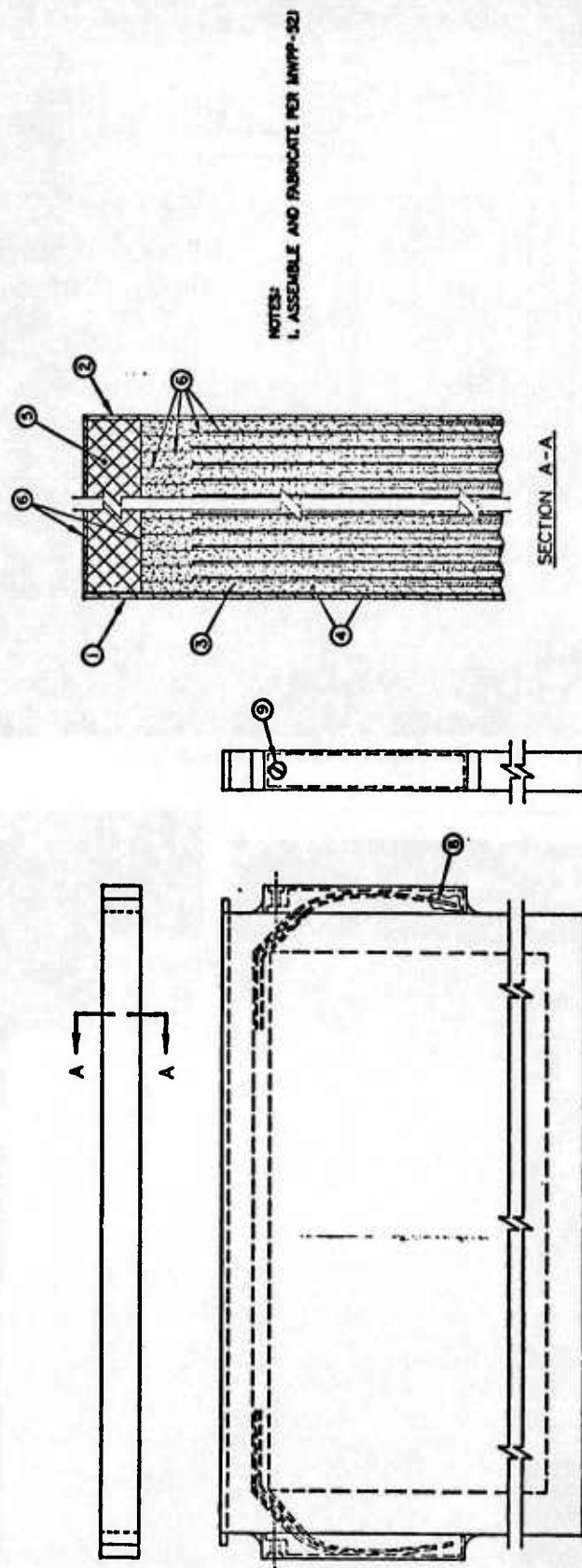


Figure 39 - Submodule Assembly

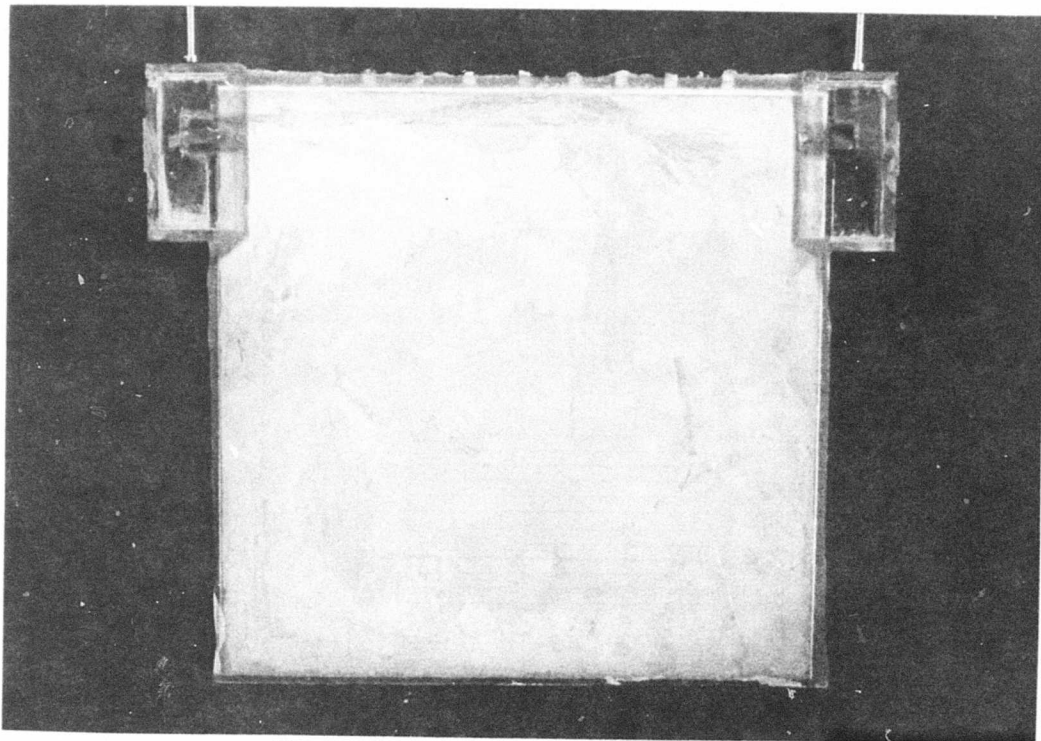


Figure 40 - Ten Cell Pile - Assembled

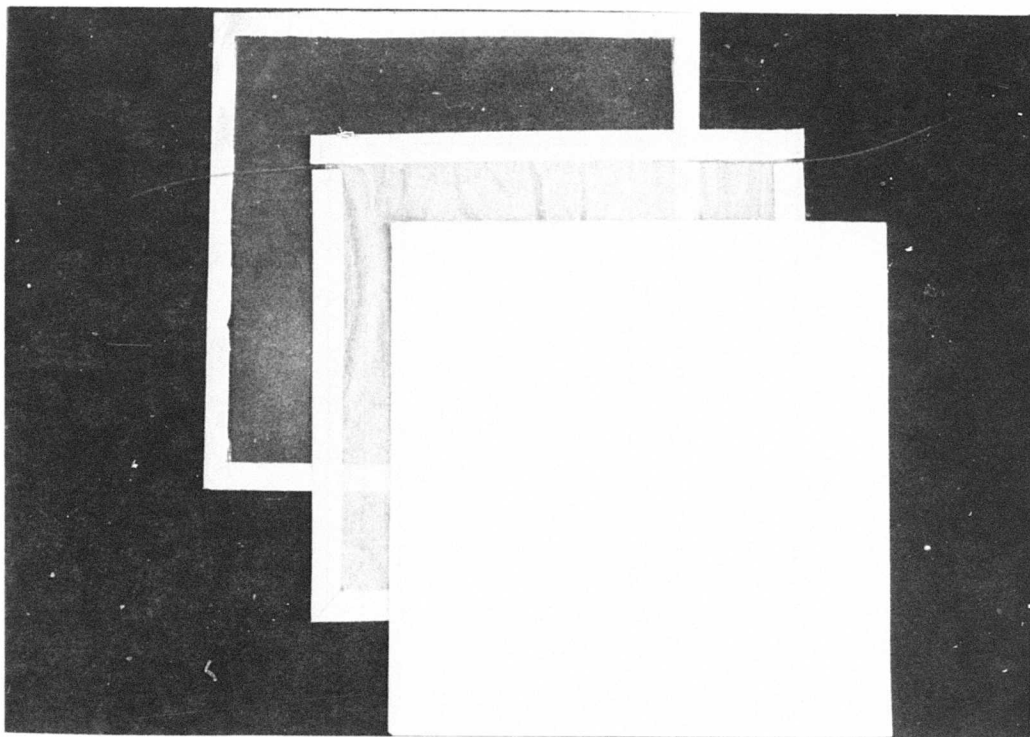


Figure 41 - Single Cell - Exploded View

5.0 Testing

Activation, testing methods, and equipment requirements covered in Paragraph 5.1 were established by the chronological development from scaled single cell piles to full scale multi-cell piles. Figure 42 is a bar chart which indicates the levels of effort and the length of time involved in each. The chart also includes the efforts on USAF Contract No. F33615-73-C-2074 which led to this contract.

Test results shown in Paragraph 5.2 represent the most current data available. Electrical performance data is shown for ten (10) cell piles as is the transient analysis. Cycle life data is cumulative in nature and the curve represents the best data attained since the start of the contract.

5.1 Operating Procedures

5.1.1 Activation

Present activation procedures for multi-cell piles are based on the performance of a number of test piles. The following steps describe the activation procedure found to be the best:

1. Clamp pile in charge/discharge test fixture.
2. Attach tubing from electrolyte reservoirs to the pile sumps.
3. Place a pre-measured amount of electrolyte in each reservoir.
4. Place reservoirs and pile in a vacuum chamber and pull 25 in. Hg for one (1) hour.
5. Release vacuum and allow pile to stand at atmospheric pressure for 15 minutes.
6. Measure electrolyte volume in reservoirs and record.
7. Repeat steps 4, 5 and 6 once a day for three (3) days or until desired electrolyte volume is in the pile.
8. Let pile stand for a minimum of three (3) days from first activation.

- 9, Remove reservoirs and record final electrolyte volumes accepted.

5.1.2 Charge

Present charging procedures for a ten (10) cell full scale pile require a low rate formation charge with higher rate consecutive charges.

The formation charge follow the proceeding steps:

1. Connect pile to charging panel and set power supply for constant current operating mode.
2. Charge pile at 5 ma/in^2 rate for twenty (20) hours or 19.6 volts whichever occurs first.
3. Record individual cell voltages at fifteen (15) minute intervals.
4. Disconnect pile and allow to stand with 20 in. Hg. vacuum on both sumps for one half hour minimum.
5. Record individual cell open circuit voltages and impedances.

Consecutive cycle charging is accomplished in the same manner as above with these exceptions: the charge rate is increased from 5 ma/in^2 to 10 ma/in^2 and the pile is charged to a 19.6 volt cutoff voltage.

Figure 43 is an equipment block diagram of the charging system. It is capable of charging ten, full scale (i.e. 40 cells) submodules. Figures 44 and 45 are photographs of the actual mechanical and electrical equipment required to accomplish charging ten full scale submodules.

5.1.3 Discharge

A present discharge for a ten (10) cell, full scale pile is accomplished with a fixed resistant load. When single current densities or voltages are discussed, they represent the nominal fifteen (15) second values, unless otherwise specified. The procedure for discharge follows these steps:

1. Apply 5 psi pressure to each sump on the pile and allow time for the pile to fill with electrolyte.
2. Detach pressure/vacuum lines and record individual cell open circuit voltages and impedances.
3. Connect load cables and current and voltage monitoring leads.
4. Discharge for thirty (30) seconds or until cell reaches 12.0 volts at 1.75 amps/in².
5. Record individual cell voltages and pile voltage and current.
6. Attach pressure/vacuum lines to sumps and pull 20 in. Hg. for a minimum of one half hour.

Presently, the first four (4) discharge cycles are used to condition the cells. The first discharge rate is 0.25 amps/in² and the rate increases with consecutive cycles until 1.75 amps/in² is reached on the fifty cycle.

Figure 44 and 45 are photographs of the charge/discharge equipment and Figure 46 is a block diagram describing its interconnection.

5.2 Test Results

5.2.1 Electrical Performance

While problems were encountered, primarily in the cycling of the ten (10) cell piles, good performance data has been attained. Figure 47 is typical discharge curves for ten cell piles subjected to current densities ranging from 1.3 amps/in² to 1.91 amps/in². Assuming the nominal load voltage to be the fifteen (15) second voltage, regulation of the battery voltage was maintained between +2.0% and -6.0% for all current densities shown. Pulse discharging on a five (5) second period and a 40% duty cycle did not change the voltage regulation. Figure 48 is a discharge curve showing open circuit voltages and load voltages for a pile that was pulse discharged for an accumulated 30 seconds at 1.4 amps/in².

5.2.4 Pile Failure Analysis

The failure analysis of about fifty (50) multi-cell piles has revealed five (5) specific problem areas which have contributed to poor performance on a given cycle and poor cycle life capability. The five (5) problem areas are:

1. Trapped gas
2. Excessive activation gas
3. Negative seal surface
4. Gas removal between cycles
5. Cell unbalance

Trapped gases between the layers of cellophane separator appears to occur during construction. The gas pockets reduce the active surface area in the cell and the cell has poor voltage during discharge. Two (2) possible solutions are being considered, laminated separator and vacuum curing of the finished multi-cell stack.

Excessive activation gas is evolving from the negative electrode and is causing weak cell discharge voltages due to reduced surface area. Beaker tests have shown that these gases bubbles form and stay on the surface of the negative electrode, and without an effective vent system remain there. Negative electrode additives, electrolyte additives, an improved vent system or any combination of the three (3) are being explored as possible solutions as described in previous paragraphs.

The failure of the negative seal surface causes external cell shorts. The failure is attributed to the negative electrode gasing discussed above and the possible solutions are the same.

Failure to remove gases between cycles cause a gradual reduction in cell capacity on each consecutive cycle. The vent system presently being used is the cause of the problem and improved vent systems are being designed and tested.

5.2.2 Transient Analysis

Two (2) transient tests were conducted, the first from 0 - 50 micro-seconds and the second from 0 - 50 milli-seconds. The 0 - 50 micro-second test was conducted to allow the determination of its effect on output electronics. Figure 49 is a trace of voltage versus time in microseconds for a ten cell pile discharged at 1.5 amp/in^2 . The plateau from ten (10) to twenty (20) microseconds is apparently the time the positive electrodes in the pile remained on the AgO level. The traces of voltage for the first fifty (50) milliseconds at various current densities is displayed in Figure 50. The primary reason for examining this transient was to determine the length of time required for the voltage to recover within -5% of the nominal load voltage (i.e. 15 second voltage). At 1 amp/in^2 and 1.5 amps/in^2 the voltages reached 95% of nominal in approximately 25 milliseconds while at the 2.4 amps/in^2 rate, it required greater than 50 milliseconds

5.2.3 Cycle Life

Difficulties were encountered in attaining adequate cycles on ten (10) cell piles. However, the reasons appear to be mechanical in nature rather than electro-chemical and are explained in more detail in Paragraph 5.2.4. Cycle life capabilities of the pile configuration has and is presently being demonstrated from 60 to 70 cycles which indicates that the present electrodes and separator system are adequate. Figure 51 is a graph of accumulated data of watts/in^2 at 15 seconds versus cycles for a pile configuration. The minimum value for power per in^2 at 15 seconds which has been determined from projections is 2.1 watts/in^2 . Cycle life of the separator system has also been demonstrated in conventional cells as high as ninety (90) cycles before failure. These tests were conducted to demonstrate capabilities of the separator without the mechanical influence of the pile configuration.

Cell unbalance in a multi-cell pile is caused primarily by all of the problems discussed above. Even if the gassing problems are minimized, it is felt that individual cell charge control will be necessary to achieve the optimum cycle life that the pile is capable of delivering.

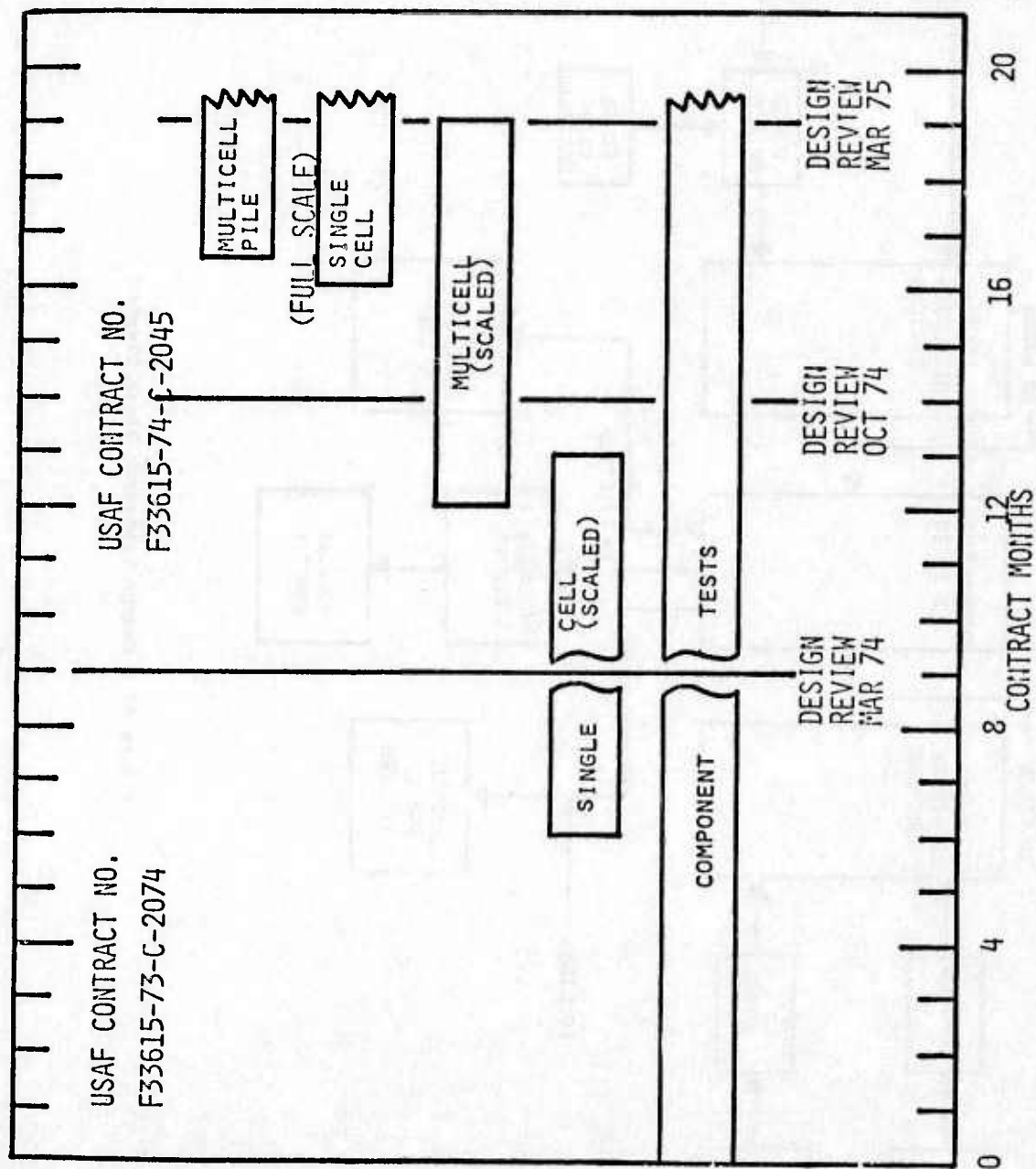


Figure 42 - Test Article Configuration

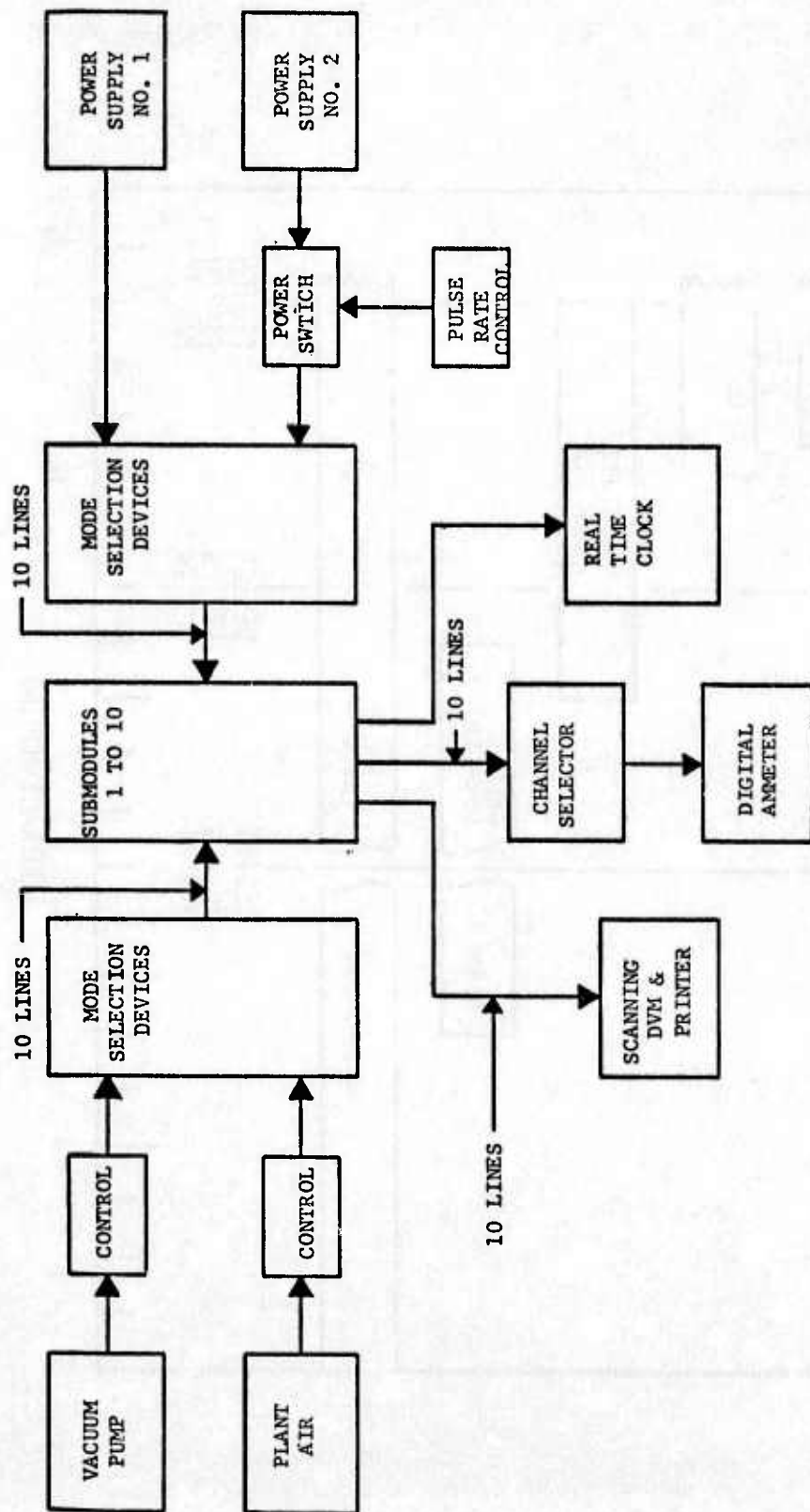


Figure 43 - Charge Equipment Block Diagram

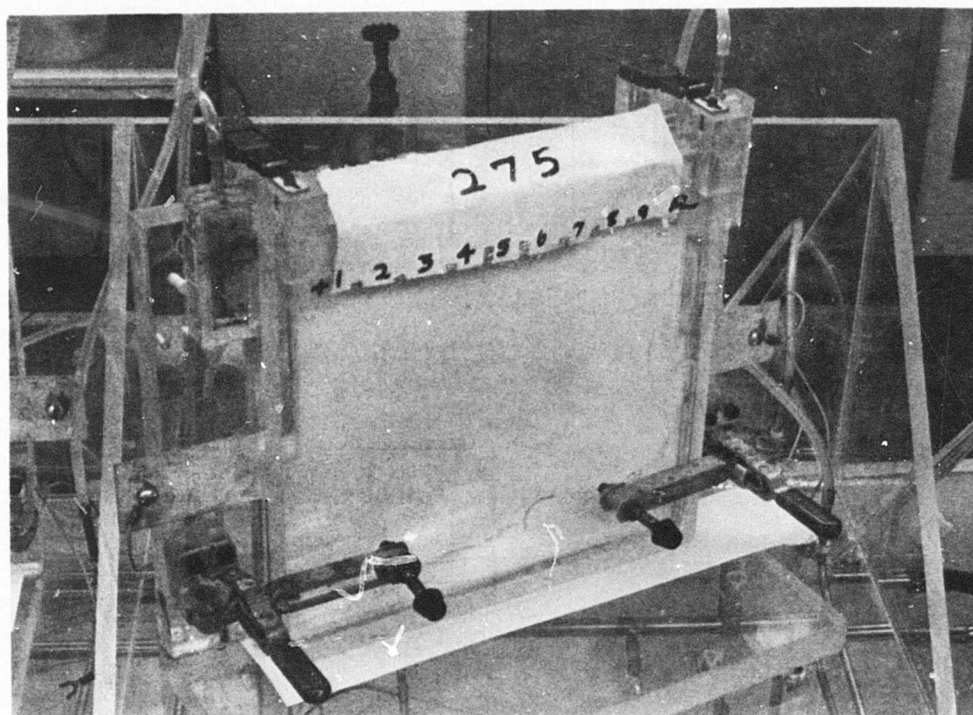


Figure 44 - Ten Cell Pile in Test Fixture

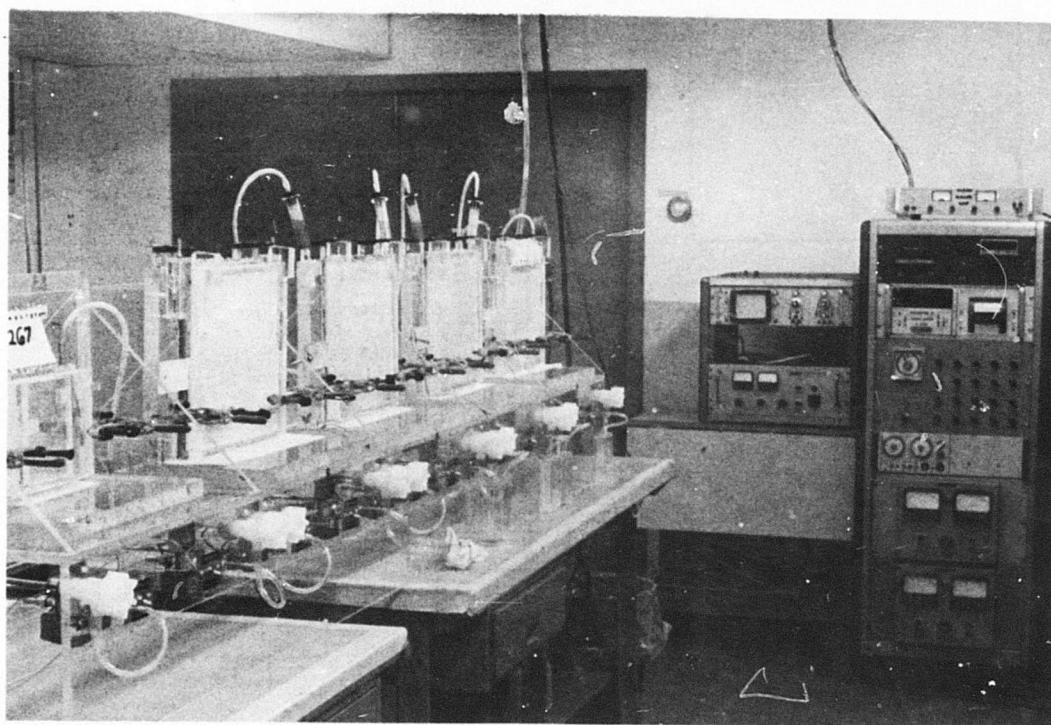


Figure 45 - Test Equipment Layout

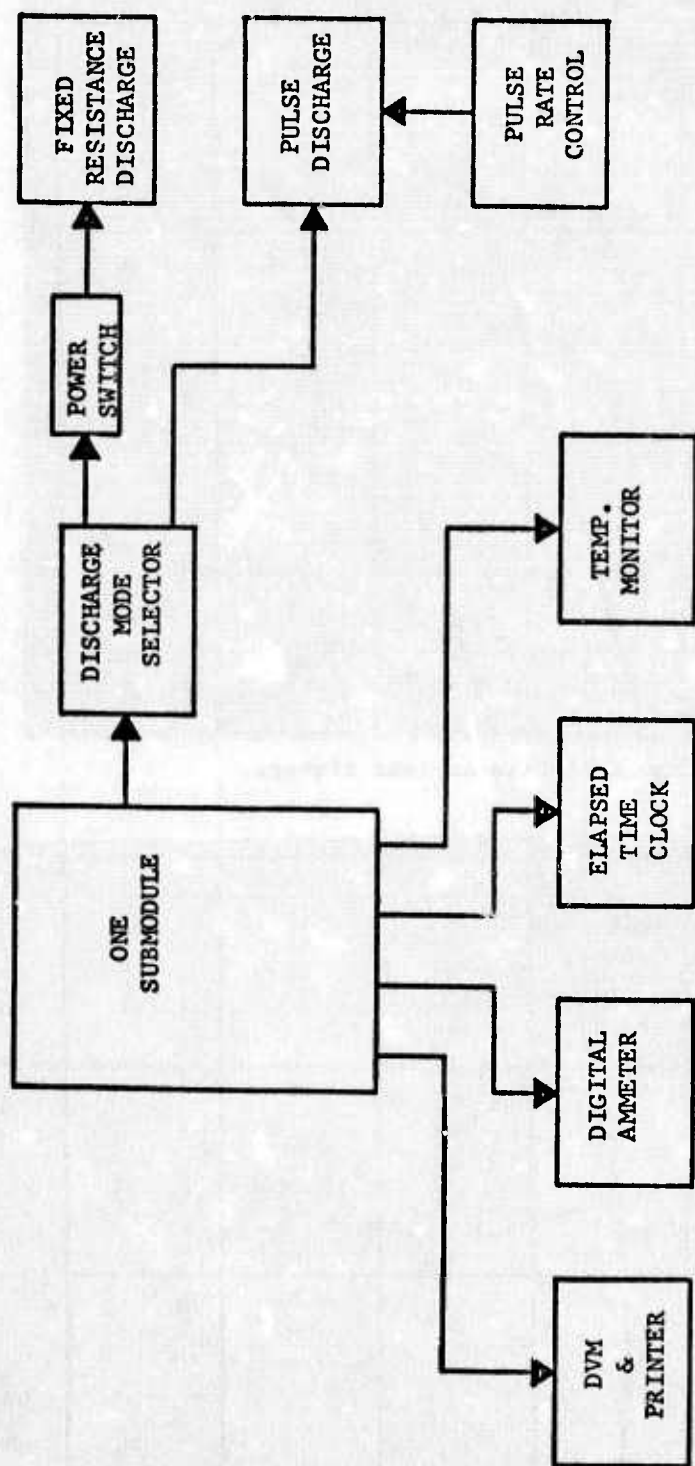


Figure 46 - Discharge Equipment Block Diagram

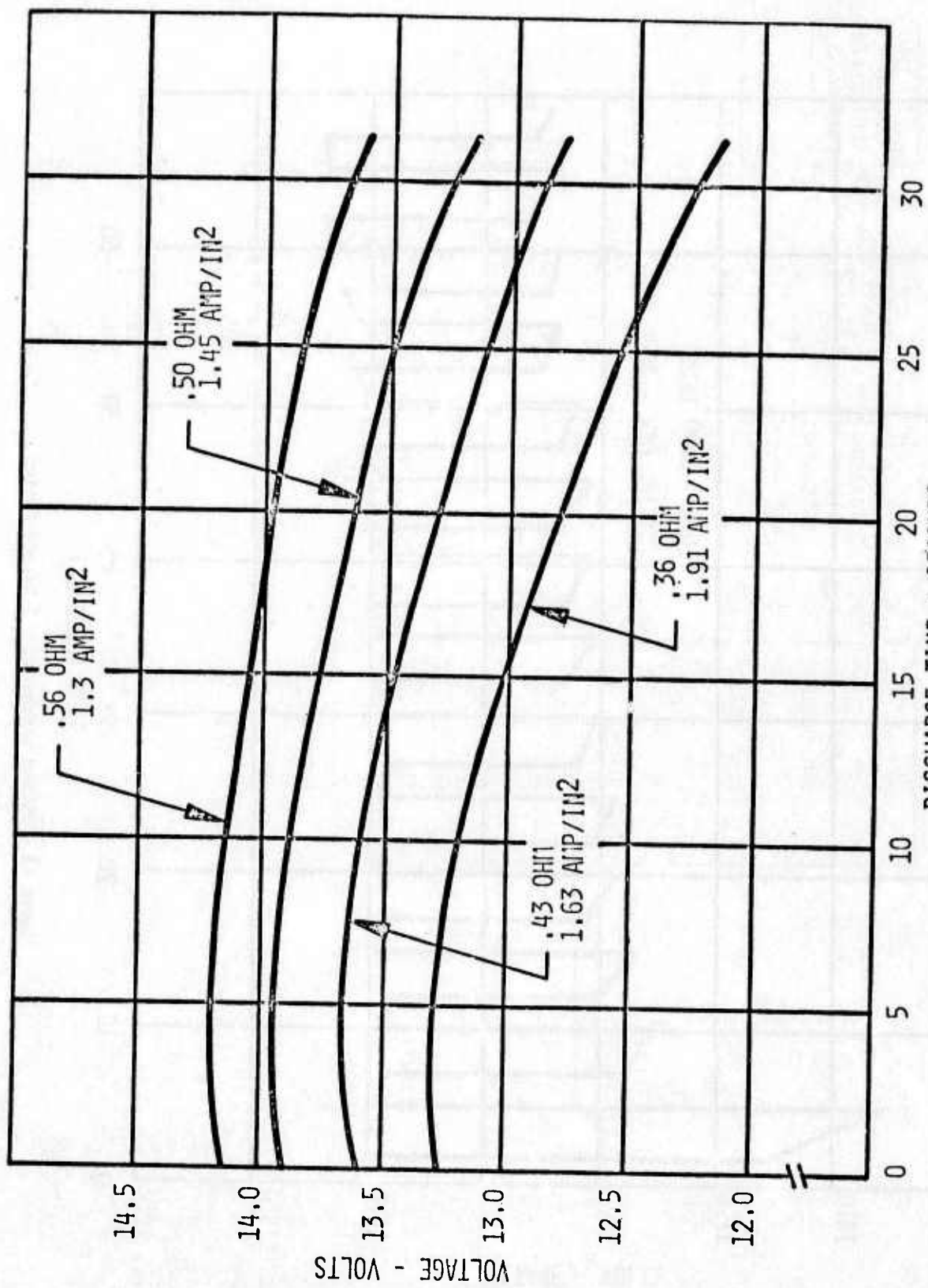


Figure 47 - Discharge Curves - Ten Cell File

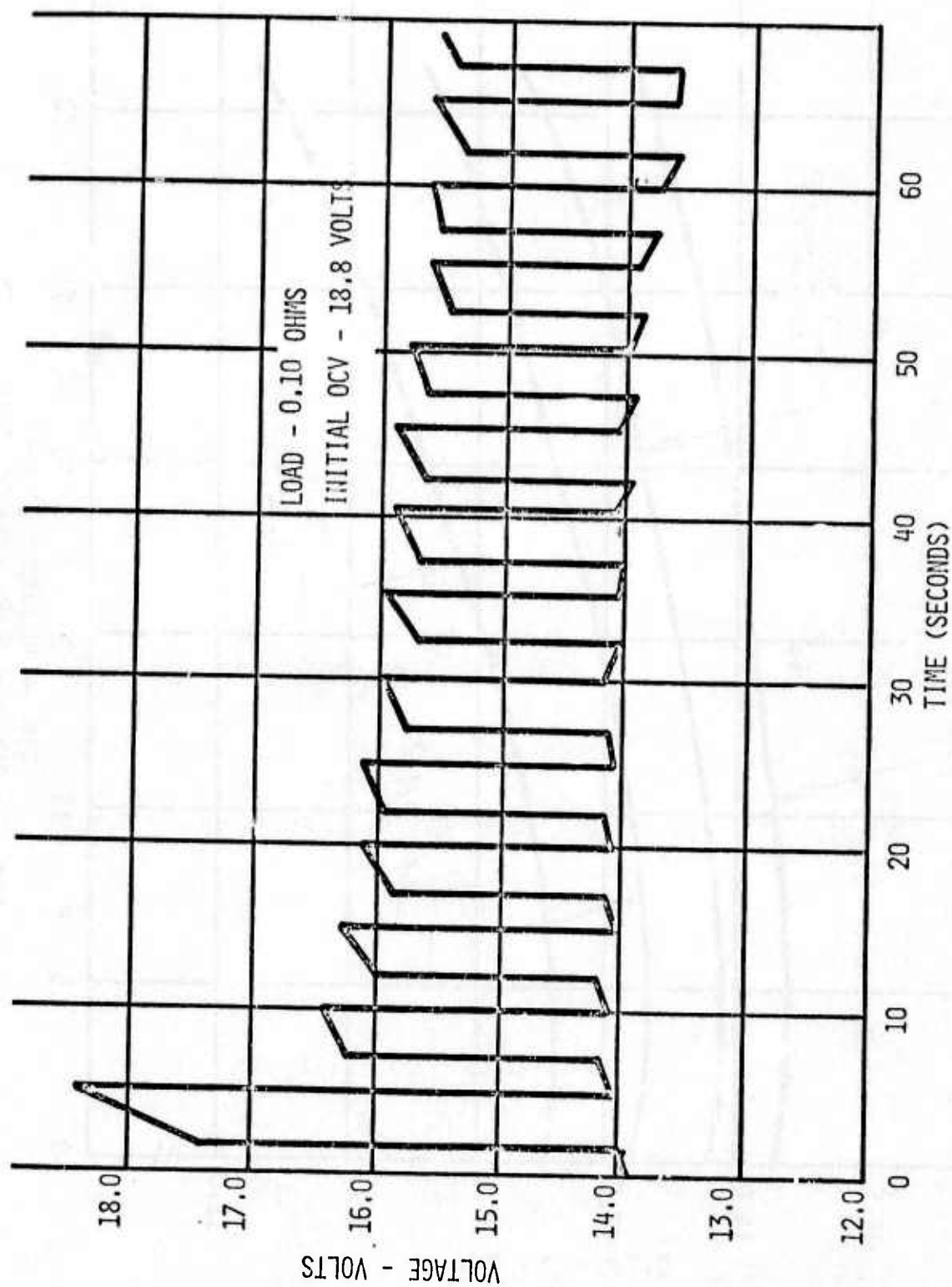


Figure 48 - Pulsed Discharge - 5 Second Period

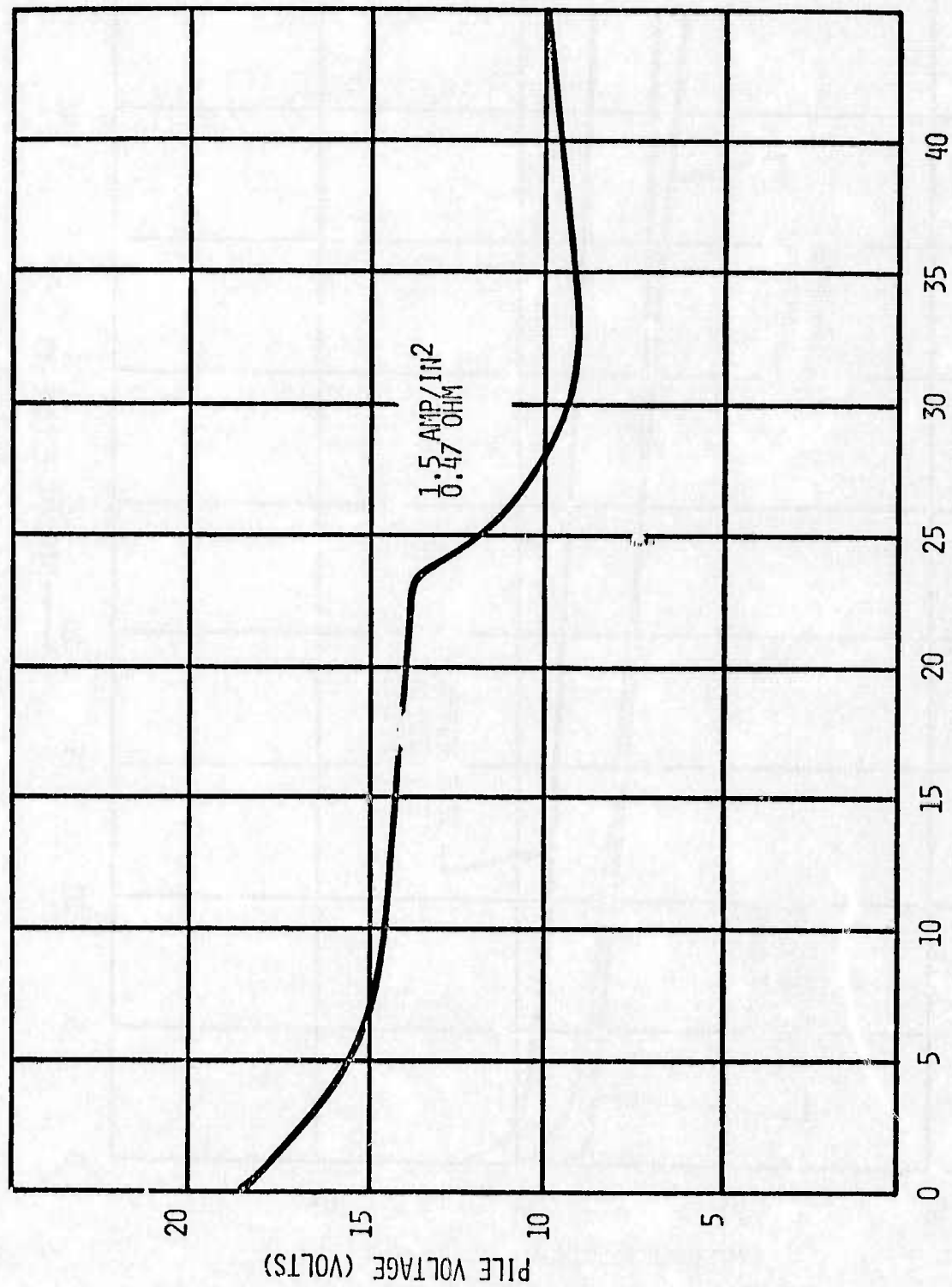


Figure 49 - 50 Microsecond Transient Curves

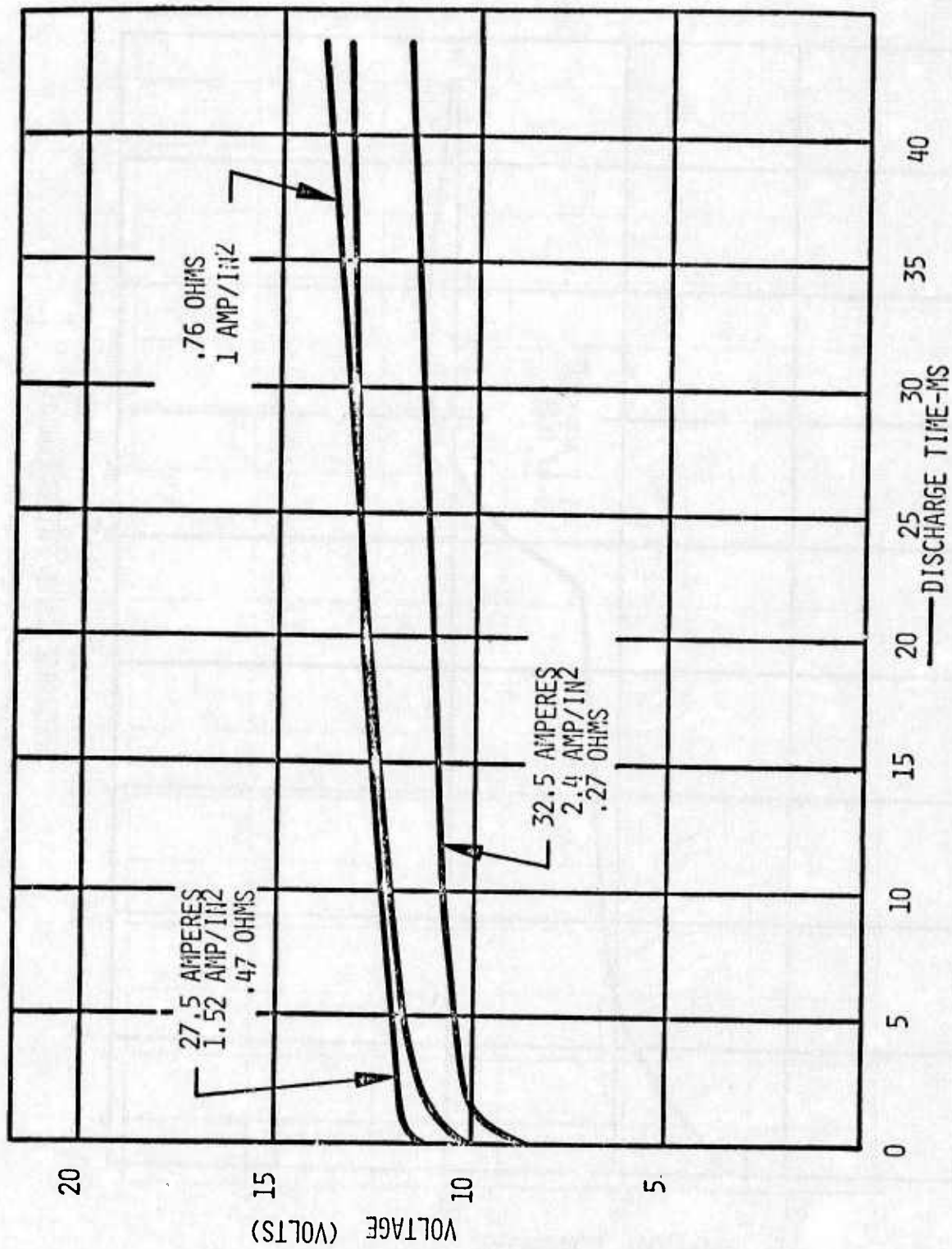
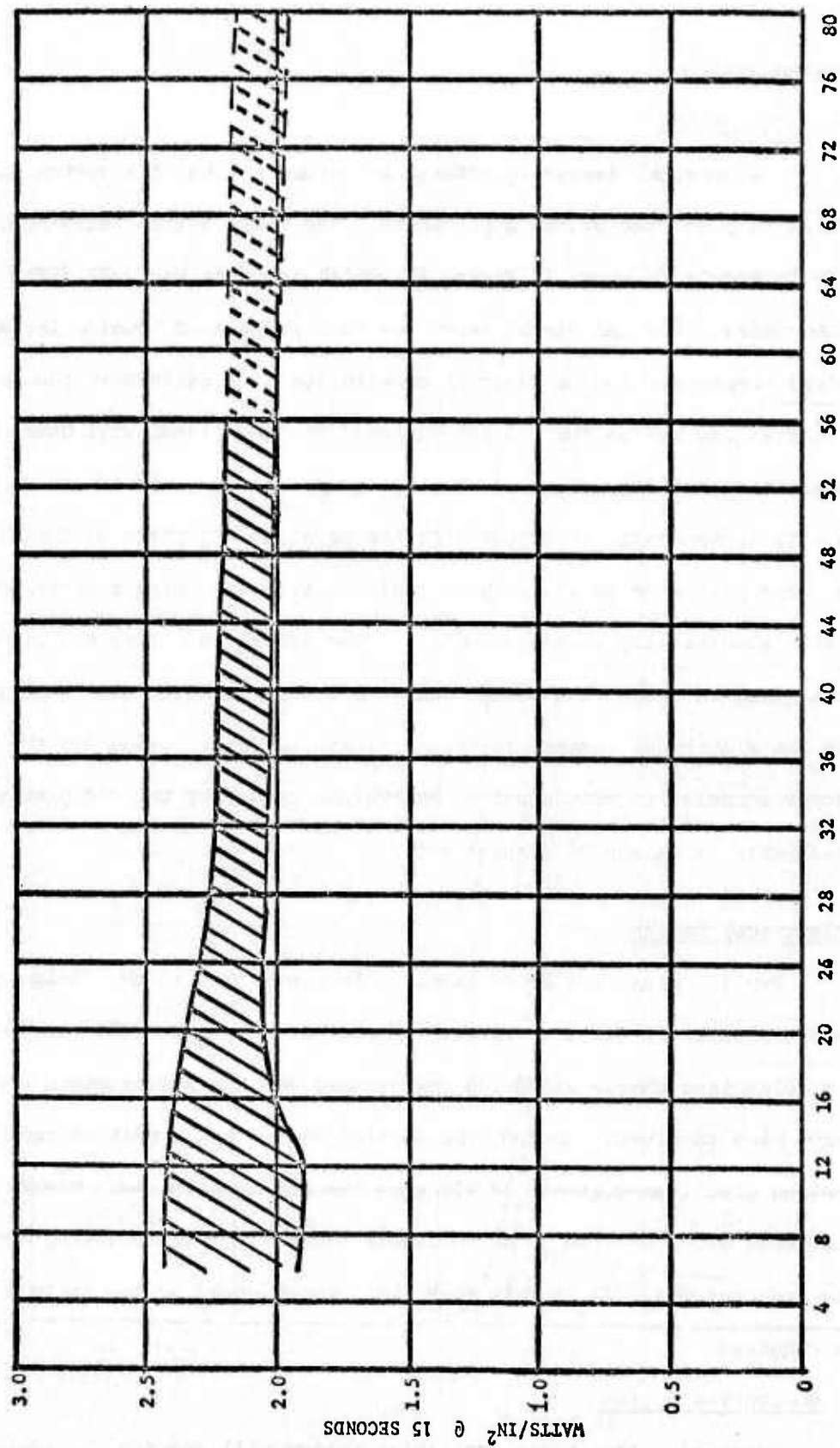


Figure 50 - 50 Millisecond Transient Curves

Average Power Per Cell vs. Cycle Life
for 30 Second Discharges
at 1.75 amps/in² Nominal



CYCLES
Cell Cycle Life Data
(Figure 51)

6.0 System Design

6.1 Physical Design

The physical design is modular in nature so that the system configuration is predicted by the application. The basic system building block is a 100 kw module as shown in Figure 52, which contains ten (10) fifty (50) volt submodules. The end plates serve the dual purpose of housing the module electrical components and in conjunction with the side rails form the physical restraining system for the submodules. The end plates will have male and female interlocking straps so that the positive end plate of one (1) module will mechanically interlock with the negative end plate of another module. End plates of an all plastic configuration are being considered along with electrically insulated metals. The latest end plate has also been minimized in weight and volume due to the determination of the physical size of the electrical components housed within. Present goals for the percentage increase in module weight and volume caused by the end plates and side rails is 11 and 30, respectively.

6.2 Electrical Design

Two (2) areas are being examined independently in the design of the module electrical system. First, the monitoring system will functionally be split into charge and discharge systems and the requirements for each have been examined. Second, the control system which must be capable of handling discharge currents of 200 amps has been considered. Figure 53 is functional block diagram of a module electrical system, including monitoring and controls. It is felt that this system would be the minimum system required.

6.2.1 Monitoring System

Presently, the charge monitoring system will require the monitor-

ing of individual cell voltages. To accomplish individual cell monitoring, each bi-polar electrode in the module will have a tab which is connected to a circuit board. D. C. board connectors will then transfer cell voltage information to either modular, discrete component, analog sensors or a scanning type central computer.

Discharge monitoring will be on a submodule level using optically isolated leads to a central controller (i.e. a micro processor). High speed scanning of submodule voltage and/or temperature will supply the necessary information for the controller to react.

6.2.2 Control System

The charge control system will function on an individual cell level and will control the charge current. A constant current power source will be supplying current to the module while individual cell currents will be reduced by a shunting device as the monitoring system predicts.

The discharge control system has required the most consideration at this point in the contract. Discharge control will be accomplished on a module level since the loss of a single module in a 20,000 volt system represents only a 2.5% decrease in system voltage.

An all series (i.e. 20,000 volt) system poses the greatest problem in removing a module from the system. It is presently felt that this control must be done during a no load condition. Two (2) devices will be required, an open circuiting device and a shunting device. Whether or not these devices will be solid state or mechanical has not yet been established. On the other hand, any system where four (4) modules could be tied in parallel a total load sharing capability exists. Only one (1) open circuiting device would be required to remove a module from the system and the

and the loss of power would be minimal since the three (3) remaining modules could carry the additional current.

6.3 Weight and Volume Projection

Data collected during this period has been used in a projection program to calculate the weight and volume characteristics of a complete module and system. As a base power level, a module of 100 kw was used for the projection to four (4) a megawatt system. These projections include packaging and system electrical interconnection as shown in the Final Technical Report (AFAPL-TR-74-37) for U.S.A.F. Contract number F33615-73-C-2074. Figure 54 shows the system projections for 100 and 400 kw modules as compared to current density. From this figure, substantial reduction in weight and volume is evident at the higher module power level. To further show the effect of the module power, Figures 55 and 56 present projection data at various current densities and module power up to 1500 kw. At approximately 500 kw, the optimum advantage is shown to exist.

Table III shows a comparison at various module power levels for the combinations shown. The first design is a projection using existing test data from multi-cell tests and shows physical capabilities in comparison to that projected. The results are within approximately 10% and are exceptionally close considering that the test cells were not purposely held to physical minimum such as the seal and sump design.

The second design is projected from the design presented herein using the median MUF for zinc as shown in Figure 14.

Number three (3) design remains the same, except Webril is used in place of the Viskon. Using a silver/zinc intercell connector replacing a solid silver foil gives the projections in design number four (4).

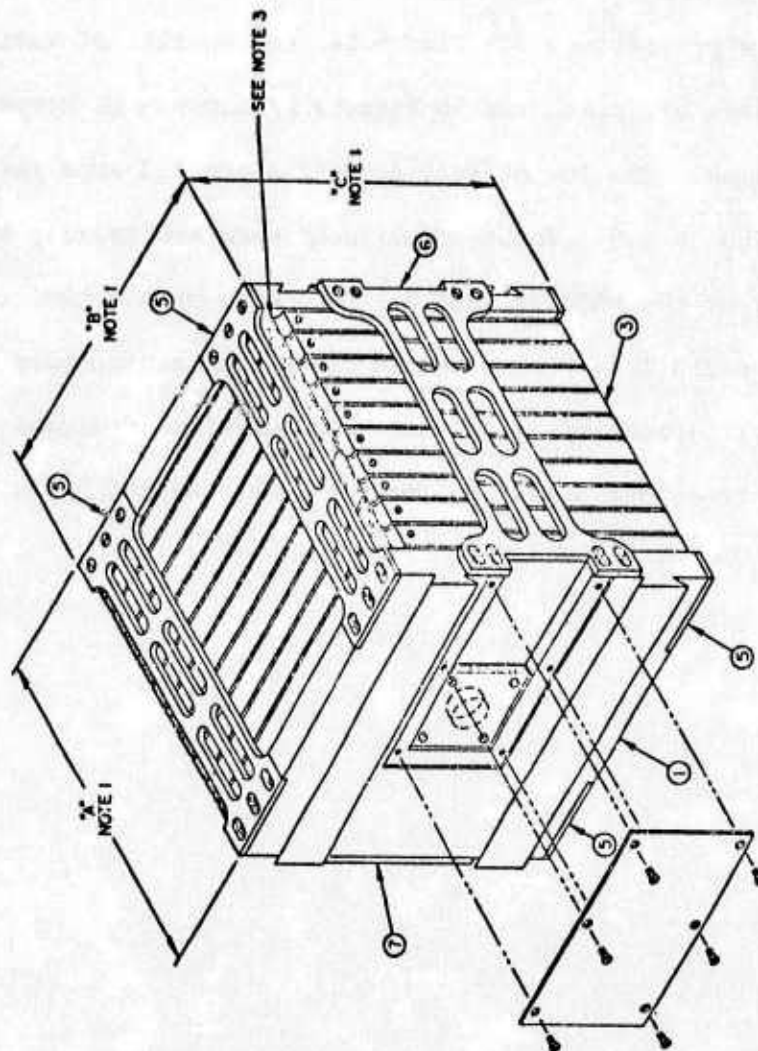
A composite projection, using the changes in 2 and 3 is shown by design number 5. The other parameters remain the same as refined number two (2).

A comparison considering the high range zinc MUF of Figure 13 is shown in the sixth design versus the refined design.

All of the improvements of the designs of five (5) projected with the high range zinc MUF is shown in design number seven (7).

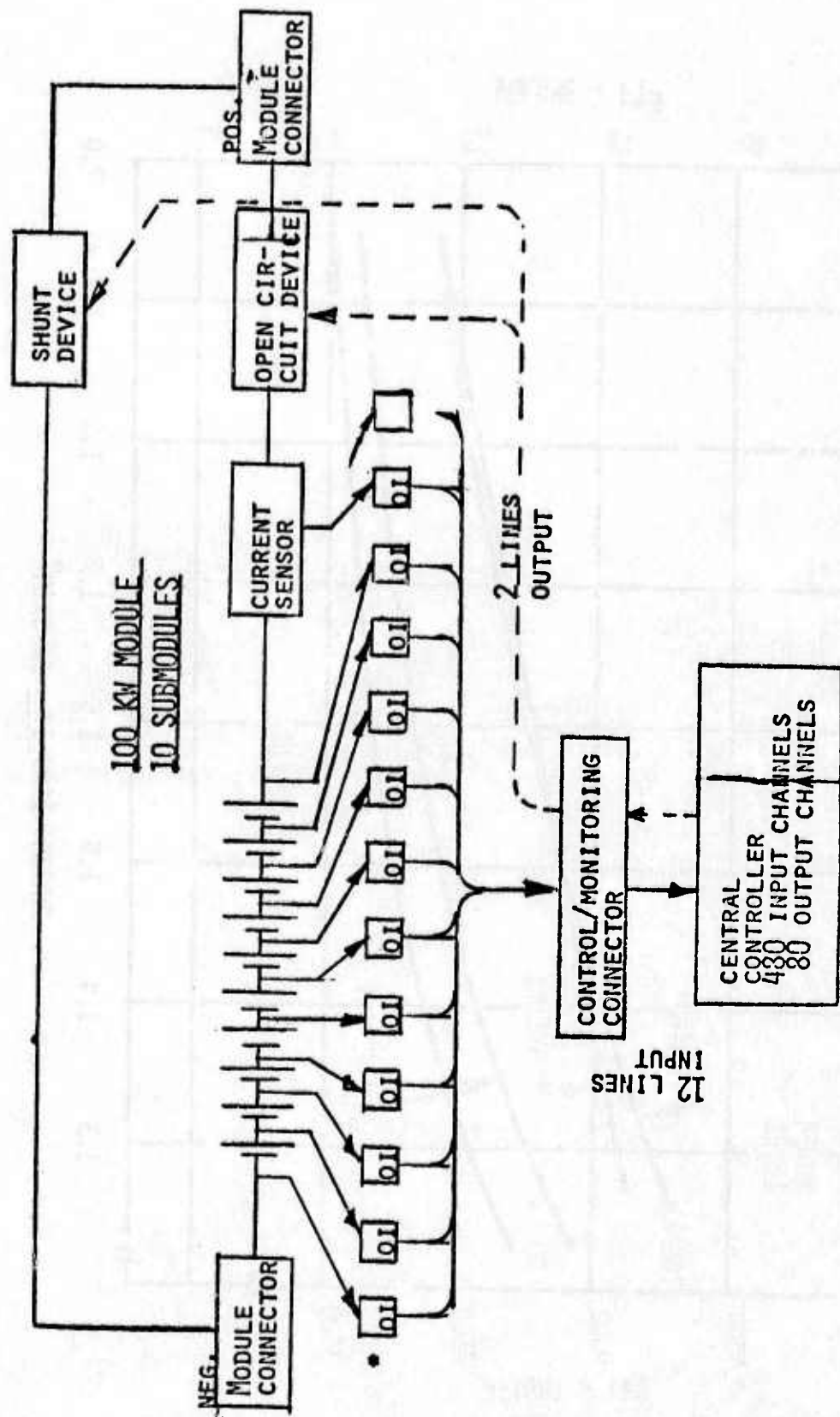
Three (3) comparisons are also shown for the above refined design and composite design number five (5) and seven (7) for 120-second discharge.

Using the projections for Figure 54, the profile of various system configurations are presented in Figures 57 through 60 compared to typical installations. The low current densities are 1.3 amps per square inch, while the high is 1.9. These comparisons were arbitrarily to demonstrate flexibility or the modular design. Depending upon actual end usage, the installations could lend themselves to other than rectangular module design; such as cylindrical cross section. No numerical comparisons have been made at this time, but appear to further reduce weight by as much as 10%.



NOTE:
 1. REFERENCE DRAWING-
 2. DIMENSIONS A, B, AND C TO BE DETERMINED BY SUBMODULE DIMENSIONS
 3. COVER CAPS NOT SHOWN BUT REQUIRED. SEE PARTS LIST FOR DETAILS

Figure 52 - 100KW Module



•NOTE: O.I.- OPTICAL ISOLATION

Figure 53 - Module Monitoring/Control System

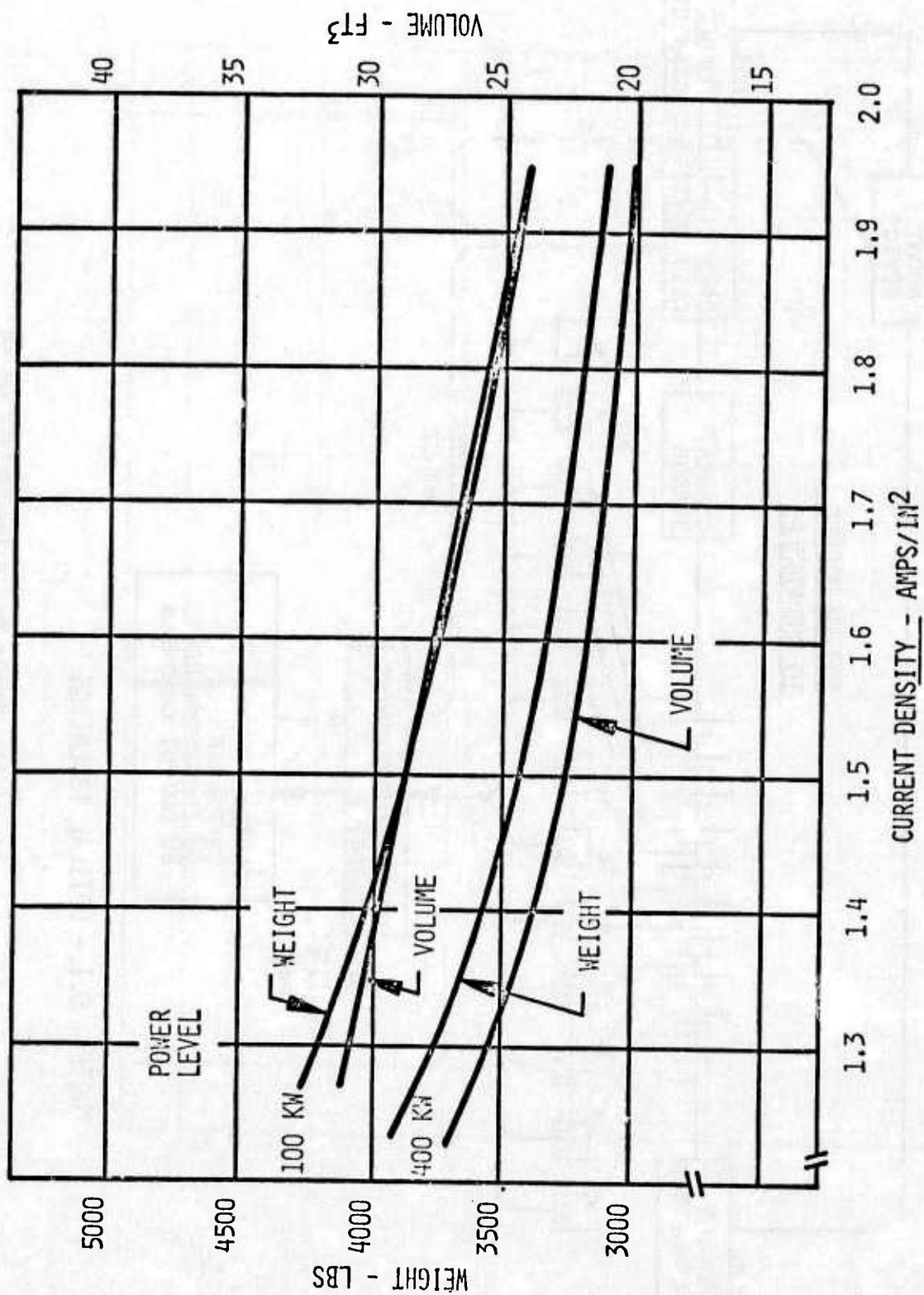


Figure 54- System Projection, Current Density vs. Weight and Volume



Figure 55 - System Projection, Module Power vs. Weight

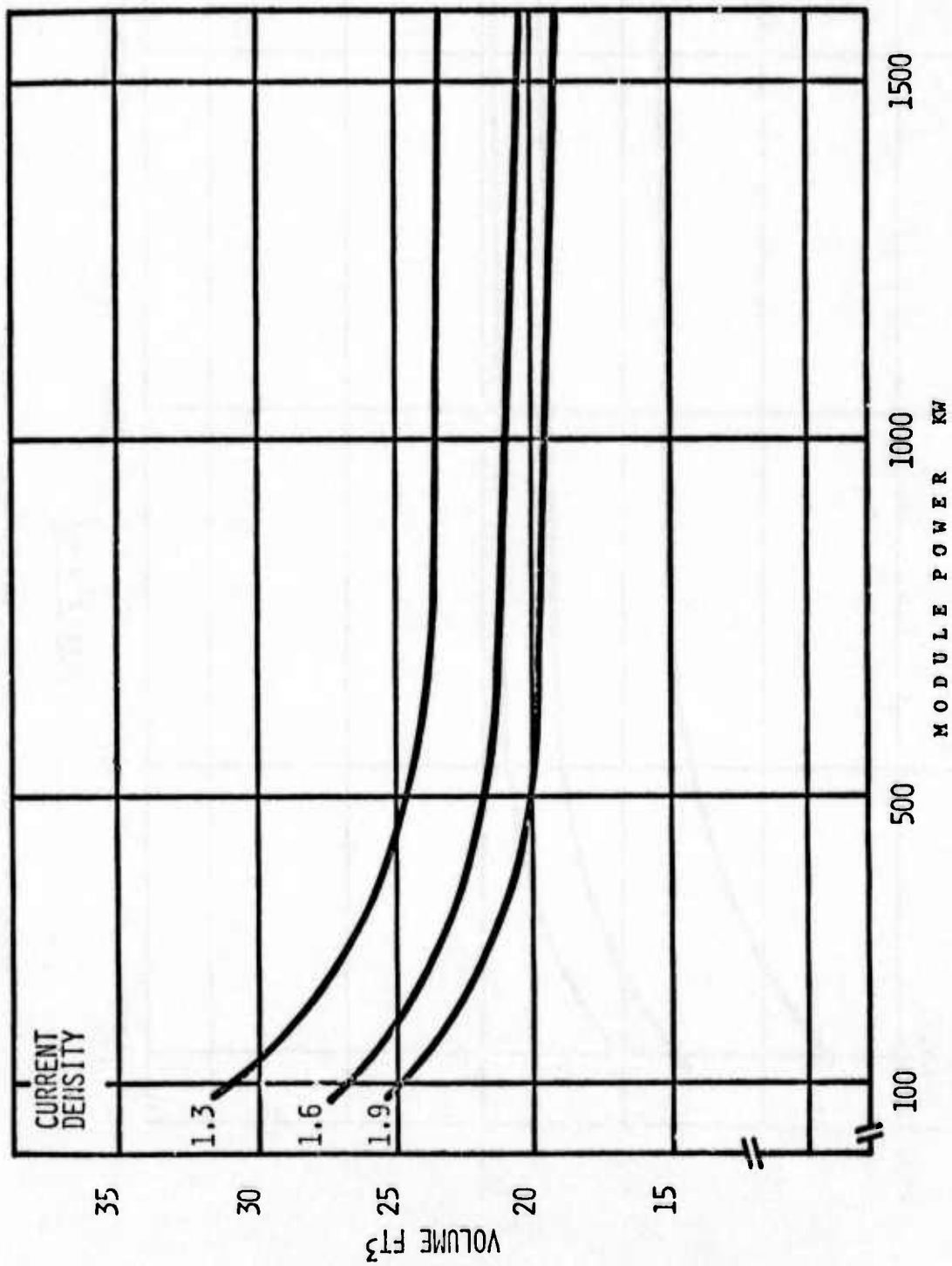


Figure 56 - System Projection, Module Power vs. Volume

TABLE III
SYSTEM WEIGHT AND VOLUME PROJECTIONS
FOUR (4) MEGAWATT
1.75 AMPS/IN²-30 SECOND DISCHARGE

	MODULE POWER		
	100 KW WT/VOL	200 KW WT/VOL	500 KW WT/VOL
1. TEST DATA PROJECTIONS			
2. REFINED DESIGN (MEDIAN RANGE Zn)	4076/30.6	3833/27.3	3687/25.3
3. SEPARATOR IMPROVEMENT	3816/26.4	3572/23.0	3289/19.8
4. INTERCELL CONNECTOR (Ag/Zn LAMINATE)	3648/25.1	3405/21.8	3259/19.8
5. COMPOSIT (PROJECTION 2, 3 AND 4)	3684/26.4	3441/23.1	3295/21.1
6. Zn IMPROVEMENT (HIGH RANGE)	3517/25.1	3273/21.8	3127/19.8
7. COMPOSIT 5 AND 6	3760/26.1	3517/22.8	3371/20.8
8. TWO (2) MINUTE DISCHARGE	3444/24.8	3201/21.5	3055/19.5
REFINED DESIGN	6435/37.5	6192/34.2	5907/31.0
COMPOSIT 5	6136/36.2	5892/32.9	5747/31.0
COMPOSIT 7	5846/34.8	5602/31.5	5457/29.6

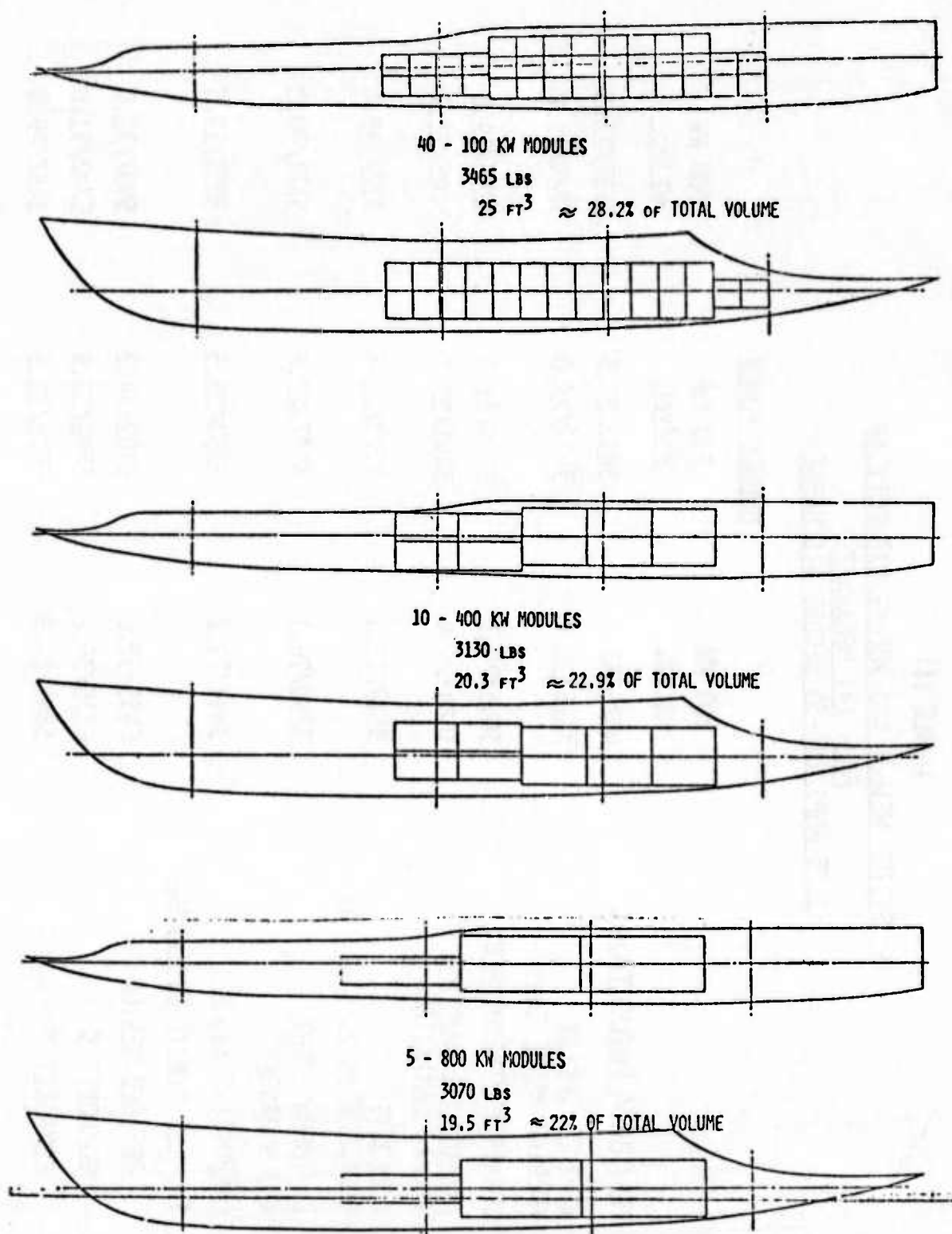


Figure 57 - Four Megawatt Battery Installations
High Current Density

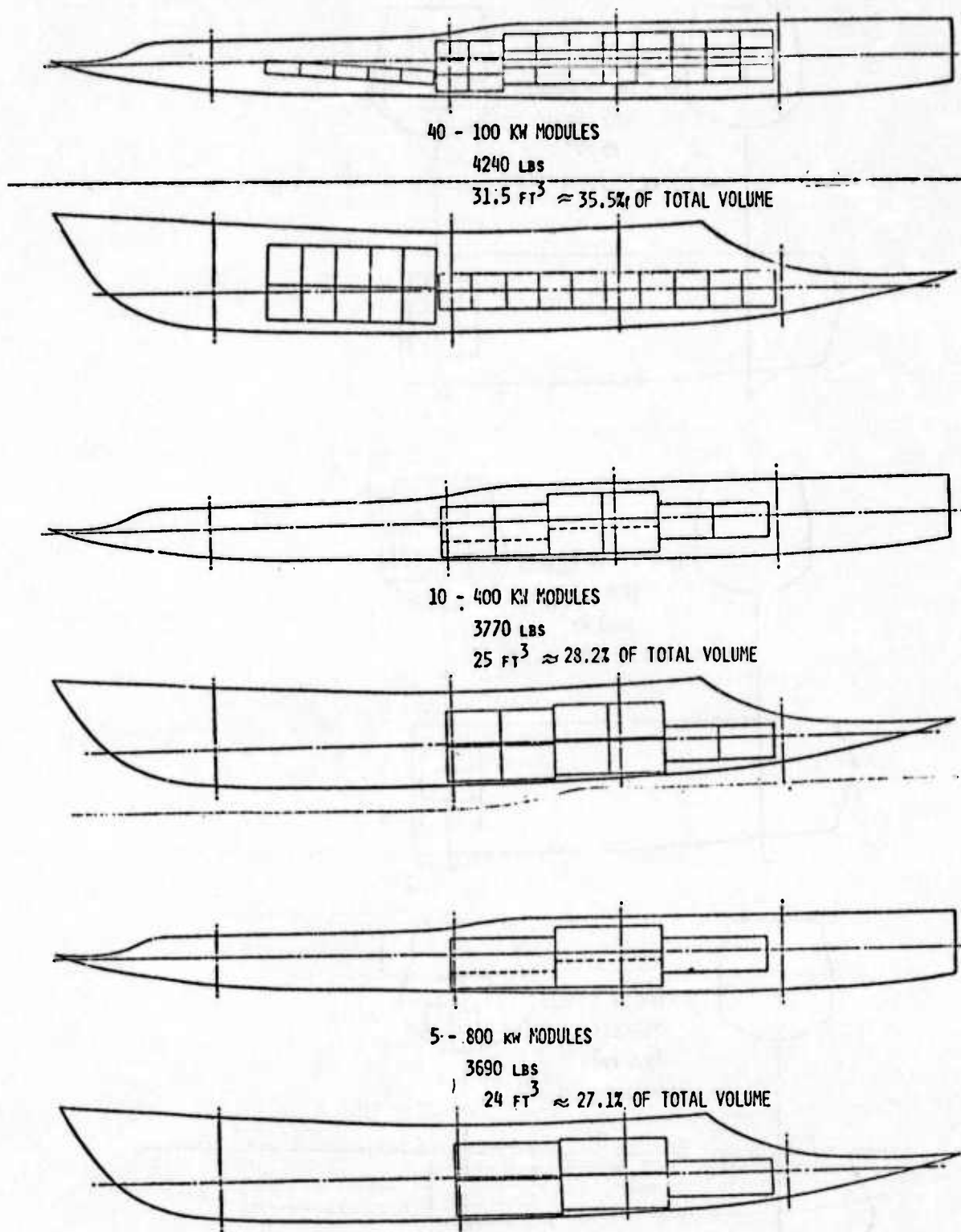


Figure 58 - Four Megawatt Battery Installations - Low Current Density

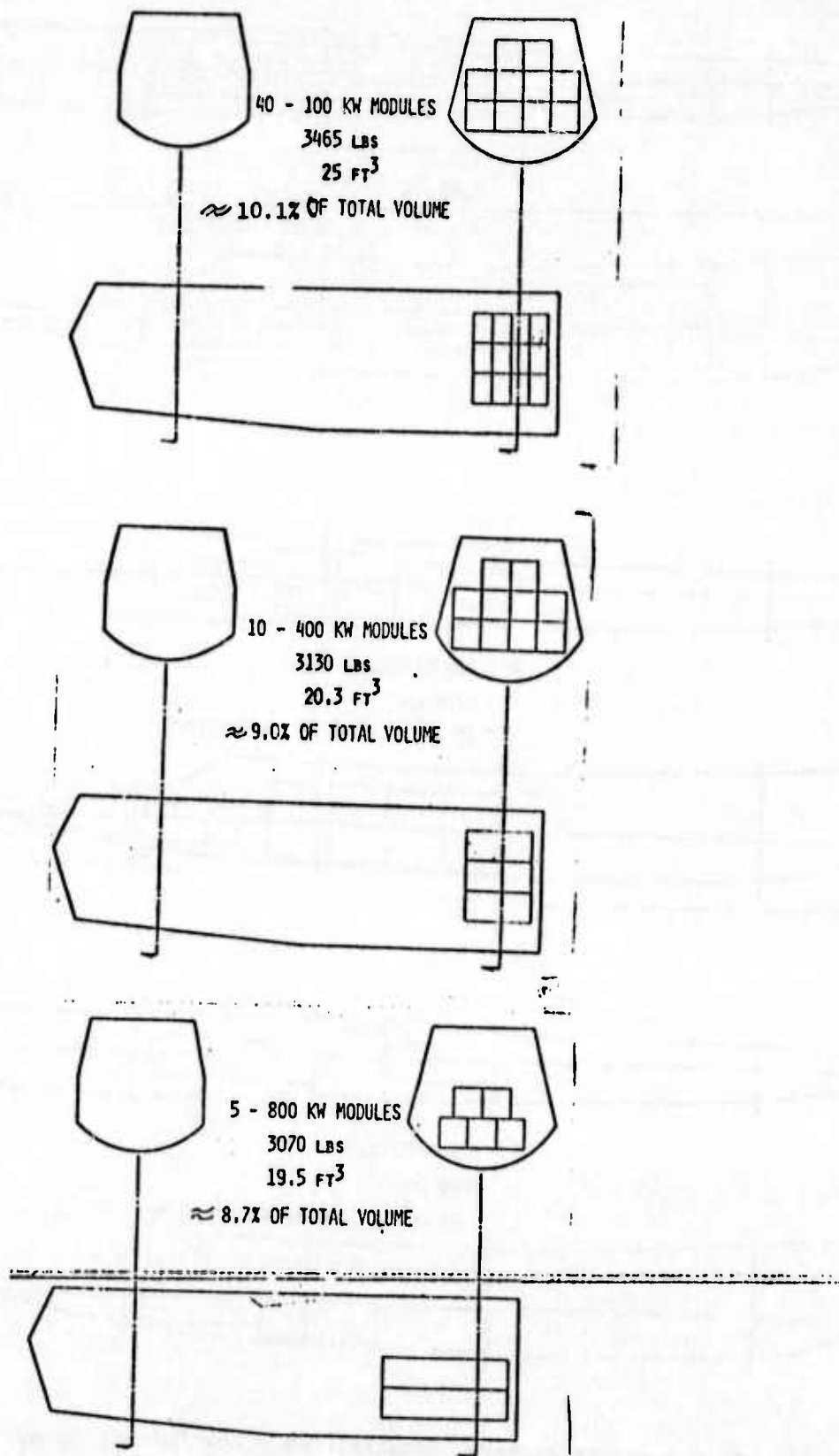


Figure 59 - Four Megawatt Battery Installations - High Current Density

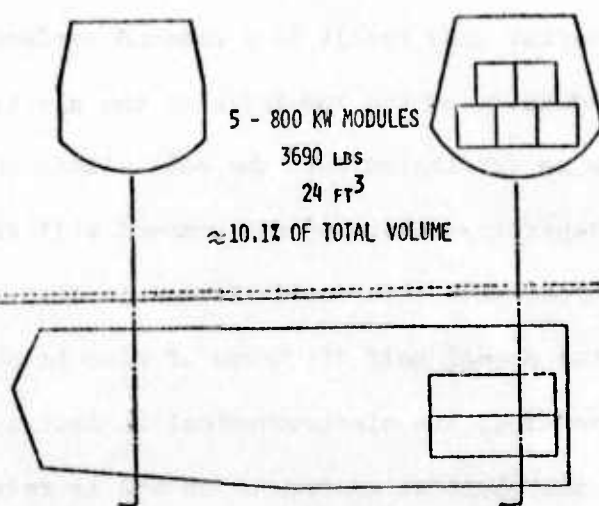
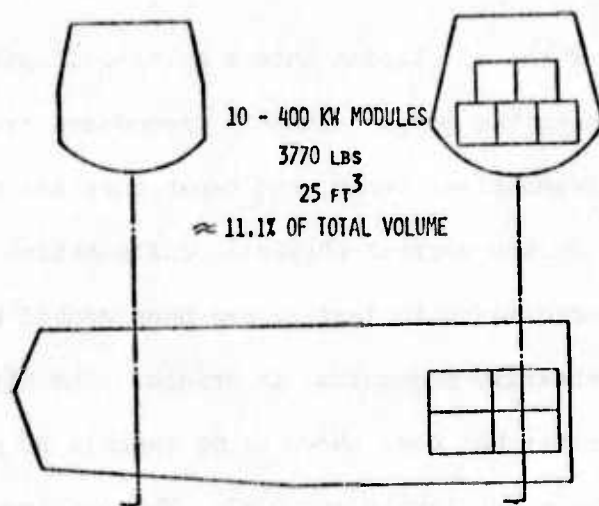
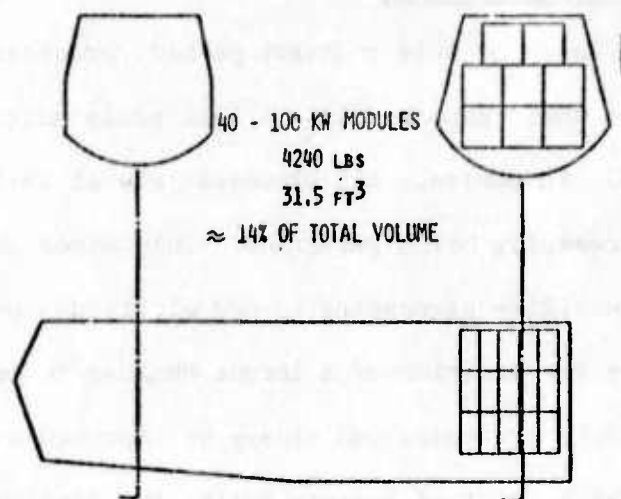


Figure 60 - Four Megawatt Battery Installations - Low Current Density

7.0 Conclusions and Recommendations

At the conclusion of this contract period, processing for producing bipolar electrodes and their assembly into a full scale multi-cell pile has been accomplished. In general, all processes are at this time sufficient to support the work presently being performed. Only minor changes would be required to increase positive processing to 600 electrodes per hour. The negative would require the addition of a larger chamber to provide large scale capabilities. Both processes can always be improved and "cleaned up" and will continue to be a point of concern during the remainder of the contract.

Fabrication of the electrodes into a multi-cell pile is relatively straight forward, assuming the proper assembly procedures are adhered to. Preparation of the seal/adhesive, vents, and separators are mainly a process of proper material use in the correct physical configuration.

Electrical performance in testing has been masked by problems which are considered to be primarily mechanical in origin. The bipolar electrode, seal/adhesive and separator has been shown to be capable of producing a complete cell providing the power levels required. The problems which do exist are associated with internal cell gases and their reduction and/or removal. Gases in the active material area result in a reduced surface area thus increasing the current density of the remainder of the electrode. A considerable amount of gas is fabricated into the cell within the free volumes of the electrodes and separators which if not removed will also reduce the active surface area. Along with this residual, gas is also formed during charge, discharge and the normal self discharge of zinc in potassium hydroxide. Even though these areas are electrochemical in nature, the problem is greatly magnified from the physical configuration and is referred to as

mechanical. Both the positive and negative possess primarily a two (2) dimension surface area, since the active materials are less than .003 inch in both cases. Even the overall cell thickness is less than .020 inch.

The recommended approach to minimize the gas problem is reduce the residual gas by mechanical approaches and the electrochemical gas by the use of additives either to the electrolyte and/or the zinc active material. The mechanical methods include such areas as electrode channeling, spacers, and an improved vent system.

The modular concept remains as the basic system design approach and provides the flexibility of designing optimum arrangements as the end use requirements become available. No major problems in the module design, other than those associated with high voltage sections are foreseen at this time. The high voltage of the module does pose problems with instrumentation and safety and handling, however, should be no more difficult than the remainder of the system, allowing for development technology from both internal and external sources.

Projection of the multi-cell piles data into four (4) megawatt systems gives weights and volumes of 3,050 to 3,800 pounds and 19.5 to 26.4 cubic feet, depending on the final module power level design.

In the following contract months, additional component development is needed to overcome the gasing problems. With this area resolved, the remainder of the multi-cell design appears to be a viable approach and will be verified as the scheduled program progresses resulting in the final contract objective, a full scale module.